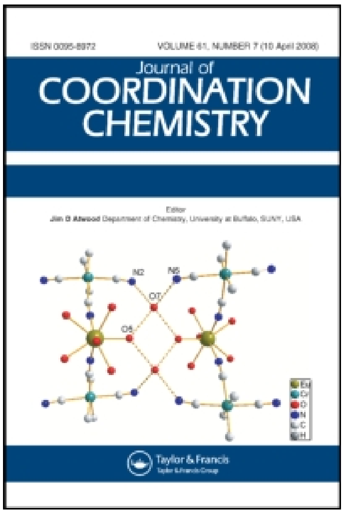

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DIMERIC MOLECULES IN THE CRYSTALS OF CALCIUM COMPLEX WITH PYRIDINE-3,5-DICARBOXYLATE LIGAND

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The crystals of di[pentaquo(pyridine-3,5-dicarboxylato, O,O′)]dicalcium(II) dihydrate contain dimeric molecules in which two Ca(II) ions are bridged by carboxylate oxygen atoms donated by only one carboxylic group of each ligand molecule [Ca–O 2.443(2) and 2.340(1) Å]. The sevenfold coordination around each Ca(II) ion is completed by oxygen atoms of five water molecules with Ca–O bond distances ranging from 2.392(2) to 2.429(2) Å. The coordination around the Ca(II) ion is a distorted pentagonal bipyramid. A network of hydrogen bonds operating *via* two hydration water molecules is responsible for the stability of the crystal.

Keywords: Pyridine-3,5-dicarboxylic acid; Calcium complex; X-ray diffraction crystal structure analysis

INTRODUCTION

The crystals of the majority of calcium(II) complexes with pyridine and pyrazine carboxylate ligands which have been studied by X-ray diffraction show polymeric molecular patterns. Ca(II) ions have been found to be bridged by carboxylate oxygen atoms and in some compounds also by water oxygen atoms displaying a variety of bridging modes [1, 2]. Recently we have undertaken systematic studies of Ca(II) complexes with pyridine dicarboxylate ligands in order to investigate how relative positions of potential chelating sites in the ligand molecules influence the choice of molecular

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patterns observed in the crystals. In this paper we report the results of an X-ray diffraction structural investigation of the Ca(II) complex with pyridine-3,5-dicarboxylate (3,5-PDDC or dinicotinate). It follows our previous study of the crystal and molecular structure of a Ca(II) complex with pyridine-3,4-dicarboxylate (cinchomeronate) ligand [1]. It is also a part of a series of papers reporting the crystal structures of Ca(II) complexes with pyridine dicarboxylate ligands [3].

EXPERIMENTAL

The title compound was obtained in hot aqueous solution by reacting 1 mmol of pyridine-3,5-dicarboxylic acid (ALDRICH) with 1 mmol of

TABLE I Crystal data and structure refinement details for $Ca_2(3,5\text{-PDDC})_2(H_2O)_{10}\cdot 2H_2O$

Empirical formula	$C_{14}H_{30}N_2O_{20}Ca_2$
Formula weight	626.56
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	trioclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 8.012(2)$ Å $b = 9.221(2)$ Å $c = 10.420(2)$ Å $\alpha = 106.33(3)^\circ$ $\beta = 105.01(3)^\circ$ $\gamma = 109.66(3)^\circ$ $V = 640.23$ Å^3
Z	2
Calculated density	1.626 gcm^{-3}
$\mu(MoK\alpha)$	0.54 mm^{-1}
$F(000)$	330.0
Crystal size	$(0.3 \times 0.2 \times 0.5)$ mm^3
Max 2θ for data collection	59.94°
Index range	$-11 \leq h \leq 10$, $-12 \leq k \leq 12$, $0 \leq l \leq 14$.
No. of measured reflections	2973
No. of reflections with $F_o > 4\sigma(F_o)$	2557
R_{int}	0.0235
Method of structure solution	direct method
Method of structure refinement	full-matrix least squares on F^2
No. of parameters refined	233
Goodness-of-fit on F^2	1.090
Final $R1$ $[F_o > 4\sigma(F_o)]$	0.0301
Final $wR2$ index	0.0863
Absorption correction	ψ-scan
Min. and max. transmission factors	0.575, 0.641
Largest diff. peak and hole	0.35 e/Å^3 and -0.53 e/Å^3
Weight parameters (A, B)	0.0584. 0.01
Mean shift/esd	0.073

calcium nitrate tetrahydrate. After boiling the solution for one hour it was left at room temperature. Colorless, rectangular single crystals were found in the mother liquid after a couple of days. The dimensions of the crystal taken for data collection are given in Table I, together with other details of the experiment. 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 atoms were located by direct methods using the SHELXLS program [4] and hydrogen atoms then found by successive Fourier

TABLE II Fractional atomic coordinates and equivalent isotropic displacement(Å^2) for $Ca_2(3,5\text{-PDDC})_2(H_2O)_{10} \cdot 2H_2O$

Atom	*X*	*Y*	*Z*	*Ueq*
Ca	1.08679(4)	0.78500(4)	1.12513(3)	0.0196(1)
C2	0.8021(3)	0.3521(2)	0.5145(2)	0.0266(3)
C3	0.8236(2)	0.5007(2)	0.6148(2)	0.0200(3)
C4	0.7629(2)	0.6051(2)	0.5624(2)	0.0203(3)
C5	0.6815(2)	0.5578(2)	0.4127(2)	0.0200(3)
C6	0.6636(3)	0.4056(2)	0.3218(2)	0.0265(3)
C7	0.9158(2)	0.5489(2)	0.7762(2)	0.0222(3)
C8	0.6121(2)	0.6662(2)	0.3508(2)	0.0223(3)
N	0.7229(2)	0.3038(2)	0.3697(2)	0.0312(3)
O1	0.9376(2)	0.6862(2)	0.8614(1)	0.0300(3)
O2	1.0299(2)	0.5515(2)	1.1849(1)	0.0347(3)
O3	0.6436(2)	0.8075(2)	0.4368(1)	0.0370(3)
O4	0.5241(2)	0.6062(2)	0.2142(I)	0.0295(3)
O5	1.3168(2)	0.7111(2)	1.0441(2)	0.0311(3)
O6	1.3896(2)	0.9298(2)	1.3313(2)	0.0374(3)
O7	1.2120(3)	1.0409(2)	1.0918(2)	0.0433(4)
O8	1.0204(2)	0.9471(2)	1.3124(2)	0.0436(4)
O9	0.7418(2)	0.6758(2)	1.0449(2)	0.0329(3)
O11	0.2925(3)	0.9888(2)	0.8330(2)	0.0469(4)
H2	0.836(3)	0.274(3)	0.545(2)	0.031(5)
H4	0.768(4)	0.709(3)	0.630(3)	0.044(7)
H6	0.604(3)	0.364(3)	0.221(3)	0.039(6)
H11	0.377(8)	1.060(7)	0.894(6)	0.13(2)
H12	0.295(5)	0.904(4)	0.773(4)	0.08(1)
H51	1.383(4)	0.686(3)	1.107(3)	0.051(7)
H52	1.246(4)	0.627(4)	0.973(3)	0.045(7)
H61	1.472(5)	0.896(4)	1.360(3)	0.062(9)
H62	1.423(6)	1.011(5)	1.377(4)	0.08(1)
H71	1.225(6)	1.015(5)	1.018(5)	0.10(2)
H72	1.182(5)	1.120(4)	1.111(3)	0.063(9)
H81	1.109(5)	1.029(4)	1.396(3)	0.058(8)
H82	0.920(5)	0.972(4)	1.284(3)	0.055(8)
H91	0.670(4)	0.610(3)	0.960(3)	0.037(6)
H92	0.695(4)	0.655(4)	1.098(3)	0.055(8)

TABLE III Selected bond lengths (Å) and angles(°) for $Ca_2(3,5\text{-}PDDC)_2(H_2O)_{10} \cdot 2H_2O$

Ca(II) coordination					
Ca—O1	2.443(2)			O1—Ca—O9	69.4(1)
Ca—O2	2.340(1)			O9—Ca—O8	72.6(1)
Ca—O5	2.429(2)			O8—Ca—O6	76.5(1)
Ca—O6	2.407(2)			O6—Ca—O5	73.0(1)
Ca—O7	2.397(2)			O5—Ca—O1	77.0(1)
Ca—O8	2.399(2)			O2—Ca—O6	87.5(1)
Ca—O9	2.410(2)			O7—Ca—O6	81.2(1)
				O2—Ca—O7	168.4(1)
				O1—Ca—O2	108.8(1)
Ligand molecule					
N1—C2	1.346(2)			N1—C2—C3	123.1(1)
C2—C3	1.393(2)			C2—C3—C4	118.2(1)
C3—C4	1.391(2)			C3—C4—C5	119.4(1)
C4—C5	1.396(2)			C4—C5—C6	117.8(1)
C5—C6	1.391(2)			C5—C6—N1	123.8(1)
C6—N1	1.340(2)			C6—N1—C2	117.5(1)
C3—C7	1.512(2)			O1—C7—O2^{I}	124.6(1)
C7—O1	1.250(2)				
C7—O2^{I}	1.265(2)				
C5—C8	1.509(2)			O3—C8—O4	124.6(1)
C8—O3	1.253(2)				
C8—O4	1.267(2)				
Water molecule					
O11—H11	0.73(5)			H11—O11—H12	132(5)
O11—H12	0.85(4)				
Hydrogen bonds					
O5—H51 . . . O4^{II}	2.711(2)	H51 . . . O4^{II}	1.86(3)	O5—H51—O4^{II}	171(3)
O6—H61 . . . O3^{II}	2.776(2)	H61 . . . O3^{II}	1.93(3)	O6—H61—O3^{II}	174(3)
O5—H52 . . . O2^{I}	2.840(3)	H52 . . . O2^{I}	2.11(3)	O5—H52—O2^{I}	152(3)

O7—H71...O11$^{\mathrm{V}}$	2.882(3)	H71...O11$^{\mathrm{V}}$	2.11(4)	O7—H71—O11$^{\mathrm{V}}$	170(4)
O8—H81...O3$^{\mathrm{VI}}$	2.851(3)	H81...O3$^{\mathrm{VI}}$	1.99(3)	O8—H81—O3$^{\mathrm{VI}}$	164(3)
O9—H91...O4$^{\mathrm{IV}}$	2.817(3)	H91...O4$^{\mathrm{IV}}$	2.02(3)	O9—H91—O4$^{\mathrm{IV}}$	160(3)
O9—H92...O4$^{\mathrm{III}}$	2.835(2)	H92...O4$^{\mathrm{III}}$	2.07(3)	O9—H92—O4$^{\mathrm{III}}$	168(3)
O6—H62...O3$^{\mathrm{VI}}$	3.042(2)	H62...O3$^{\mathrm{VI}}$	2.48(5)	O6—H62—O3$^{\mathrm{VI}}$	142(4)
O7—H72...O1$^{\mathrm{VI}}$	3.105(2)	H72...O1$^{\mathrm{VI}}$	2.28(3)	O7—H72—O1$^{\mathrm{VI}}$	172(3)
O11—H11...O5$^{\mathrm{VI}}$	3.042(2)	H11...O5$^{\mathrm{VI}}$	2.41(5)	O11—H11—O5$^{\mathrm{VI}}$	143(5)
O11—H12...N$^{\mathrm{IV}}$	2.862(3)	H12...N$^{\mathrm{IV}}$	2.00(4)	O11—H12—N$^{\mathrm{IV}}$	175(3)
O8—H82...O11$^{\mathrm{VII}}$	2.910(3)	H82...O11$^{\mathrm{VII}}$	2.03(3)	O8—H82—O11$^{\mathrm{VII}}$	163(3)

Symmetry code: (I) $-x+2, -y+2, -z+2$; (II) $x+1, y, z+1$; (III) $x, y, z+1$; (IV) $-x+1, -y+1, -z+1$; (V) $x+1, y, z$; (VI) $-x+2, -y+2, -z+2$; (VII) $-x+1, -y+2, -z+2$.

syntheses. Final refinement by least squares method on a set of all unique reflections was done on positional parameters of all atoms, anisotropic temperature factors of all non H-atoms and isotropic temperature factors of hydrogen atoms. $R1 = 0.043$ for all 2973 unique reflections. A weighting scheme was used in the form:

$$w = 1/[\sigma^2(F_o^2) + (A^*P)^2 + B^*P], \text{ where } P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3.$$

where A, B are parameters listed in Table I. Calculations were carried out using the SHELXL97 program [5]. 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 the title compound contain centrosymmetric dimeric molecules consisting of two calcium (II) ions bridged by carboxylate oxygen atoms donated by only one carboxylate group of each ligand molecule. Figure 1 shows the molecule of the dimer with numbering of the atoms; Figure 2 illustrates how the dimers are packed in the crystal. Although each oxygen atom is monodentate, the bridging is accomplished by two Ca–O bonds with different lengths: Ca–O2 2.340(1) Å and Ca–O1 2.443(1) Å affecting the coordination geometry around the Ca(II) ion.

Apart from the above two bridging oxygen atoms, each calcium(II) ion is coordinated by five oxygen atoms belonging to water molecules with Ca–O bond lengths ranging from 2.397(2) to 2.429(2) Å (mean 2.408 Å). The coordination polyhedron around the Ca(II) ion is a strongly distorted pentagonal bipyramid. Its base is composed of the O1, O5, O6, O8 and O9 oxygen atoms. The maximum deviation from the average plane is shown by the atoms: O1 (+0.541 Å) and O9 (−0.533 Å), the minimum shift is +0.026 Å (O6). The oxygen atoms O2 and O7 constitute the apices of the pyramid: the angle O2–Ca–O7 is 168.4(1)°. Table III contains more details of this coordination geometry.

Like the structure of the Ca(II) complex with pyridine-3,4-dicarboxylate [1] only one carboxylate group participates in chelating the metal ion, the second group being active in the hydrogen bond network. The atoms of this

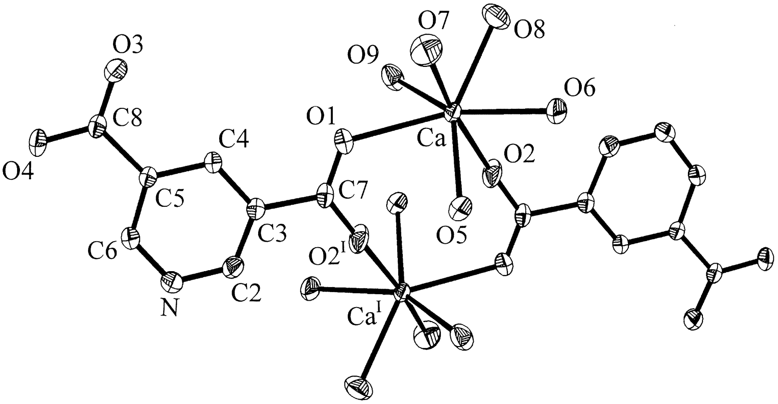

FIGURE 1 The dimeric molecule of $Ca_2(3,5\text{-PDDC})_2(H_2O)_{10} \cdot 2H_2O$ with numbering of atoms. The non-hydrogen atoms are shown at the 50% probability level.

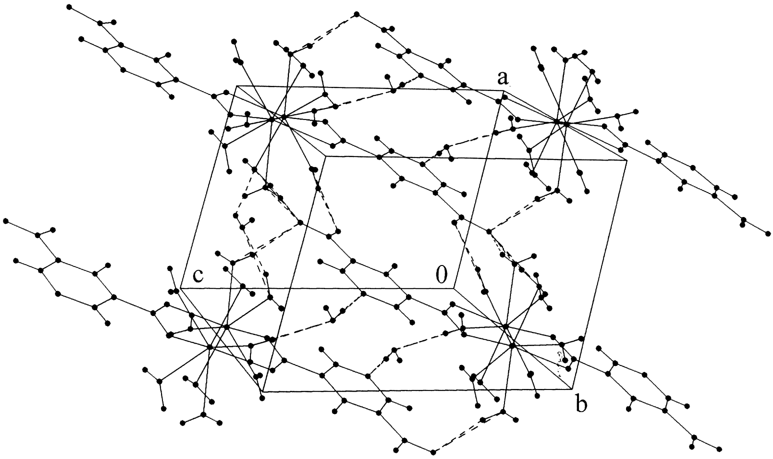

FIGURE 2 The packing diagram of $Ca_2(3,5\text{-PDDC})_2(H_2O)_{10} \cdot 2H_2O$. Broken lines indicate the hydrogen bonds.

group, the atoms constituting the pyridine ring and the atoms of the bridging carboxylate group are coplanar: the mean deviation from the best plane is 0.028 Å. The bond distances and angles observed within the title ligand molecule are in fair agreement with those reported for the parent acid [6].

The dimeric molecules of the title compound are interconnected by a network of hydrogen bonds operating between the solvation water molecules (two per unit cell), coordinated water molecules and the non-bonding carboxylate oxygen atoms. An inspection of Table III reveals that according to their lengths the hydrogen bonds can be divided into three groups. Two hydrogen bonds with the lengths 2.711(2) and 2.776(2) Å link the coordinated water molecules O5 and O6 with the "free" carboxylate oxygen atoms O4 and O3, respectively, each of them belonging to the adjacent dimer. A number of bonds with lengths in the range 2.8 to 2.9 Å can be ascribed to the second group. They link the coordinated water molecules O5, O7, O8 and O9 with the carboxylate oxygen atoms in the nearest dimers. Weak hydrogen bonds with lengths from 2.9 to 3.1 Å, which constitute the third group link coordinated water molecules with carboxylate atoms in the adjacent dimers. The solvation water molecule O11 acts as a bridge being the donor of two hydrogen bonds: one to the hetero ring nitrogen atom, the other to the coordinated water molecule, each in a different adjacent dimer. Simultaneously, the solvation water molecule is an acceptor of two bonds donated by the coordinated water molecules of another neighboring dimer (see Tab. III).

Dimeric molecules have also been found in the structure of a calcium(II) complex with pyridine-2,6-dicarboxylate [3]. This ligand shows the same geometrical shape as the ligand of the title compound, however, the bridging mode and the coordination around the metal ion were found to be entirely different. The dipicolinate molecule is coordinated to the Ca(II) ion as a tridentate ligand using one oxygen atom of each carboxylate group and the hetero ring nitrogen atom for chelating. The oxygen atom of one carboxylate group is monodentate, the oxygen atom belonging to the other group of the same ligand is bidentate being also bonded to another Ca(II) ion, thus bridging the two metal ions to form a dimer. Apart from being coordinated by three carboxylate oxygen atoms and one hetero ring nitrogen atom, each Ca(II) ion in the dimer is coordinated by four oxygen atoms from water molecules giving rise to a coordination polyhedron resembling a pentagonal bipyramid but having eight vertices.

The analysis of geometries and Ca(II) – $O_{\text{carboxylate}}$ contacts carried out for a large number of calcium(II) complexes with carboxylate ligands has indicated that the vast majority of them exhibit sevenfold and eightfold coordination around the metal ion and the Ca(II) – $O_{\text{carboxylate}}$ bond distances in the range from 2.3 to 2.5 Å [8]. The Ca(II) – O bonds and coplanarity of the carboxylate groups observed in the title compound and the Ca(II) ion fit the results of this analysis.

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