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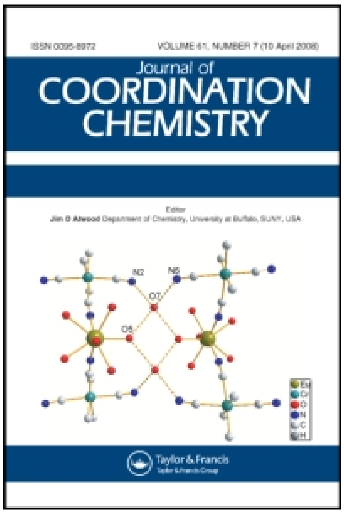

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THE CRYSTAL AND MOLECULAR STRUCTURE OF A NEW CALCIUM(II) COMPLEX WITH PYRIDINE-2,6-DICARBOXYLATE, WATER AND NITRATE LIGANDS

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Crystals of {*catena*-[μ-aqua-O]bis[μ-pyridine-2,6-dicarboxylato-O,N-O′]} {[monoaqua-nitrato, O-calcium(II)] [diaqua-calcium(II)]} contain dimeric units composed of two calcium(II) ions and two ligand molecules, in which the calcium ions are bridged by two bidentate oxygen atoms, each donated by one carboxylic group of the ligand. The Ca(II) ion is also coordinated by one oxygen atom of the second carboxylate group and the hetero-ring nitrogen atom belonging to the same ligand molecule. The dimers form molecular chains through protons situated at the symmetry centers halfway between the non-bridging carboxylate oxygen atoms. In addition, both calcium ions in the dimer are bridged to calcium ions in adjacent dimers – each by a pair water oxygen molecules giving rise to two-dimensional molecular sheets. Coordination of the Ca ion in the dimer is completed either by two water oxygen atoms or by one water oxygen atom and an oxygen atom donated by a nitrate group. The molecular sheets are held together by an extended system of hydrogen bonds.

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

INTRODUCTION

Calcium(II) ion forms a number of complexes with pyridine-2,6-dicarboxylate (2,6-PDDC or dipicolinate) ligands. All of them also contain water as a ligand. However, in one case, a nitrate ligand has been observed to be coordinated to the Ca(II) ion. One of the complexes denoted as "calcium dipicolinate trihydrate" contains dimeric units composed of two Ca(II) ions and two ligand molecules. These Ca(II) ions are bridged by two bidentate oxygen atoms donated by only one carboxylate group of each 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]. The crystal structure of a second complex called "calcium dipicolinate sesquihydrate" was not determined [1]. Dimeric molecules in which two Ca(II) ions are bridged by carboxylate oxygen atoms and the H_2(2,6-PDDC) molecules located in the crystal space have been reported in another complex [2]. The crystals of two polymorphic forms of a complex which

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contains molecular ribbons with Ca(II) ions bridged by carboxylate oxygen atoms having water and nitrate ligands attached to the metal ion have been recently obtained and their structures determined [3]. Continuing our studies on calcium(II) complexes with pyridine dicarboxylate ligands, we have obtained single crystals of one more complex with pyridine-2,6-dicarboxylate, water and nitrate ligands. The results of the x-ray diffraction study of its crystal structure are reported in this paper.

EXPERIMENTAL

The title compound was obtained by mixing hot aqueous solutions, one containing 1 mmol of calcium nitrate tetrahydrate, the other *ca.* 0.5 mmol of pyridine-2,6-dicarboxylic acid (ALDRICH). The mixture was stirred and boiled for 1 h. After a day colorless, plate-like single crystals were found in the mother liquid. Evaporation to dryness gave an amorphous material. The dimensions of a crystal selected for x-ray data collection are given in Table I.

TABLE I Crystal data and structure refinement details for Ca_2(2,6-PDDC) [H(2,6-PDDC)]$(H_2O)_5NO_3$

Compound	Ca_2(2,6-PDDC) [H(2,6-PDDC)] $(H_2O)_5(NO_3)$
Empirical formula	$C_{14}H_{17}N_3O_{32}Ca_2$
Formula weight	563.47
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P_1
Unit cell dimensions	$a = 5.870(1)$ Å
	$b = 17.790(4)$ Å
	$c = 10.600(2)$ Å
	$\alpha = 90.59(3)^\circ$
	$\beta = 96.85(3)^\circ$
	$\gamma = 91.77(3)^\circ$
	$V = 1098.39$ Å^3
Z	2
Calculated density	1.704 g cm^{-3}
μ(MoKα)	0.61 mm^{-1}
F(000)	580.0
Crystal size	0.2 × 0.2 × 0.4 mm
Max 2θ for data collection	64.00°
Index range	$-8 \leq h \leq 0$,
	$-26 \leq k \leq 26$,
	$-15 \leq l \leq 15$.
No. of measured reflections	3573
No. of reflections with $F_o > 4\sigma(F_o)$	2106
R_{int}	0.0211
Method of structure solution	direct method
Method of structure refinement	full-matrix least squares on F^2
No. of parameters refined	345
Goodness-of-fit on F^2	1.025
Final $R1$ $[F_o > 4\sigma(F_o)]$	0.0297
Final $wR2$ index	0.0877
Absorption correction	ψ-scan
Min. and max. transmission factors	0.552 and 0.667
Largest diff. peak and hole	0.30 e/Å^3 and −0.39 e/Å^3
Weight parameters A, B	0.0443, 0.00
Mean shift/esd	0.120

X-ray reflections were measured at room temperature using a KUMA KM4 (MoK_α radiation) four circle diffractometer operating in $\omega - 2\theta$ mode with two standard reflections monitored every 200 measured reflections. Lattice parameters 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. Two standard reflections were monitored every 200 reflections. Non-hydrogen ions were located by direct methods using the SHELXLS program [4] 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 $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. A, B are the parameters listed in Table I. Calculations were carried out using the SHELXL97 program [5]. Bond lengths and angles are listed in Table II. Listings of the observed and calculated structure factors and anisotropic thermal parameters can be obtained on request from the authors.

DISCUSSION

Like the case of "calcium dipicolinate trihydrate" [1], the crystals of the title compound contain molecular dimers as basic units of the structure. Each dimer is composed of two calcium ions and two ligand molecules. Figure 1 shows a dimer with numbering of atoms. The calcium ions are bridged by two carboxylate oxygen atoms (O11 and O21) acting in bidentate mode, donated by one carboxylate group of each ligand. Both Ca(II) ions are also coordinated by monodentate oxygen atoms contributed by the second carboxylate group (O14 and O24) and the hetero-ring nitrogen atoms (N1 and N2) of each ligand. All the above atoms form a plane with maximum deviations from the mean plane amounting to $+0.153(1)$ and $-0.128(1)$ Å for the Ca1 and Ca2 atoms, respectively. The environment around the Ca(II) ions also contains oxygen atoms donated by water and nitrate molecules. The water oxygen atom (O15) and nitrate oxygen atom (O31), which strongly deviate from the mean plane of the dimer [$+1.582(1)$ and $-1.555(1)$ Å, respectively], form equatorial bases of distorted pentagonal pyramids. Their apices are composed by water oxygen atoms (O16 and O31) located on opposite sides of the dimer plane. In addition, two water oxygen atoms, O17 and O27$^{\mathrm{II}}$ in the case of Ca1 ion (O27 and O17$^{\mathrm{III}}$ in the case of the Ca2 ion) are bridging the Ca ions located in adjacent dimers. The relevant bond lengths and angles are detailed in Table II. Thus, the coordination around calcium ions in the dimer of the title compound is the same as observed in the "calcium dipicolinate trihydrate" complex [1]. Both ligand molecules are planar with mean deviations from the average planes of 0.051(1) and 0.037(1) Å, respectively.

The acid ligand molecules in the dimer show bond distances and angles which are in fair agreement with those reported for the parent acid [6].

Hydrogen atoms were found to be located at the symmetry centers, halfway between two symmetry related carboxylate atoms (O13 and O13$^{\mathrm{I}}$ as well as O23 and O23$^{\mathrm{II}}$), all belonging to the non-bridging carboxylate groups of the neighboring ligand molecules. These hydrogen atoms (H11 and H21) form symmetric OHO bonds of 2.418(9) and 2.472(7) Å, respectively. Apart from maintaining the charge balance,

TABLE II Selected bond distances (Å) and bond angles (°) for $Ca_2(2,6\text{-PDDC})[H(2,6\text{-PDDC})](H_2O)_5NO_3$

Calcium ions coordination:			
Cal–N1	2.548(7)	N1–Cal–O14	65.2(2)
Cal–O14	2.490(7)	O14–Cal–O15	72.3(2)
Cal–O11	2.409(2)	O15–Cal–O21	81.5(2)
Cal–O21	2.365(8)	O21–Cal–O11	72.1(3)
Cal–O15	2.542(7)	O11–Cal–N1	61.6(3)
Cal–O16	2.435(7)	O16–Cal–N1	89.8(2)
Cal–O17	2.426(6)	O16–Cal–O15	72.9(2)
Cal–O27^{II}	2.524(7)	O17–Cal–N1	81.7(3)
		O27^{II}–Cal–N1	133.8(3)
		O17–Cal–O27^{II}	68.9(2)
Ca2–N2	2.490(8)	N2–Ca2–O24	63.4(3)
Ca2–O24	2.486(7)	O24–Ca2–O31	76.3(3)
Ca2–O21	2.515(9)	O31–Ca2–O11	90.9(3)
Ca2–O11	2.409(9)	O11–Ca2–O21	71.9(3)
Ca2–O25	2.396(9)	O21–Ca2–N2	65.0(3)
Ca2–O31	2.556(8)	O25–Ca2–N2	89.5(3)
Ca2–O27	2.440(7)	O25–Ca2–O31	71.9(3)
Ca2–O17^{I}	2.577(8)	O27–Ca2–N2	83.7(3)
		O17^{I}–Ca2–N2	133.2(3)
		O27–Ca2–O17^{I}	67.8(2)
		Ca1–O17–Ca2^{II}	111.0(3)
		Cal–O27^{II}–Ca2^{II}	112.4(3)
Coordinated water molecules:			
O15–H151	0.843(6)	H151–O15–H152	120.8(7)
O15–H152	0.850(6)		
O16–H161	0.860(6)	H161–O16–H162	110.2(7)
O16–H62	0.68(4)		
O17–H171	0.81(4)	H171–O17–H172	111.1(3)
O17–H172	0.88(4)		
O25–H251	0.98(4)	H251–O25–H252	101.5(4)
O25–H252	0.82(4)		
O27–H271	0.844(6)	H271–O27–H272	121.2(8)
O27–H272	0.846(6)		
Nitrate group:			
N3–O31	1.210(8)	O31–N3–O32	116.0(5)
N3–O32	1.235(5)	O32–N3–O33	118.3(4)
N3–O33	1.237(5)	O33–N3–O31	125.5(6)
2,6-PDDC *ligand molecules*:			
N1–C12	1.287(11)	N1–C12–C13	117.1(9)
C12–C13	1.386(13)	C12–C13–C14	124(1)
C13–C14	1.237(18)	C13–C14–C15	120(1)
C14–C15	1.488(17)	C14–C15–C16	116.3(9)
C15–C16	1.357(13)	C15–C16–N1	117.9(8)
C16–N1	1.392(9)	C16–N1–C12	124.3(7)
C17–C12	1.430(14)		
C17–O11	1.241(12)	O11–C17–O12	123(1)
C17–O12	1.236(11)		
C18–C16	1.335(13)		
C18–O13	1.315(13)	O13–C18–O14	115.4(8)
C18–O14	1.326(10)		

(*Continued*)

TABLE II Continued

N2–C22	1.382(11)			N2–C22–C23	128.1(9)
C22–C23	1.375(12)			C22–C23–C24	113.0(9)
C23–C24	1.489(15)			C23–C24–C25	118.9(9)
C24–C25	1.296(15)			C24–C25–C26	120.8(9)
C25–C26	1.406(12)			C25–C26–N2	125.7(8)
C26–N2	1.302(11)			C26–N2–C22	112.7(8)
C27–C22	1.598(12)				
C27–O21	1.297(9)			O21–C27–O22	127.8(9)
C27–O22	1.247(10)				
C28–C26	1.645(12)				
C28–O23	1.252(14)			O23–C28–O24	134.1(9)
C28–O24	1.164(11)				
Symmetric hydrogen bonds:					
O13–H11···O13^{III}	2.418(9)	H11···O13^{III}	1.209(9)	O13–H11···O13^{III}	180
O23–H21···O23^{IV}	2.472(7)	H21···O23^{IV}	1.236(7)	O23–H21···O23^{IV}	180
Interdimer hydrogen bonds:					
O17–H171–O12^{II}	2.64(1)	H172···O12^{II}	2.29(7)	O17–H171–O12^{II}	161(4)
O27–H272···O21^{I}	3.06(1)	H272···O21^{I}	2.29(7)	O27–H272–O21^{I}	151(10)
O27–H272···O22^{I}	3.07(1)	H272···O22^{I}	2.0(2)	O27–H272–O22^{I}	132(14)
O16–H162···O14^{I}	2.76(1)	H162···O14^{I}	2.0(1)	O16–H162–O14^{I}	155(13)
O16–H161···O33^{V}	2.79(1)	H161···O33^{V}	2.0(1)	O16–H161–O33^{V}	149(5)
O15–H152···O32^{V}	2.74(1)	H152···O32^{V}	2.1(1)	O15–H152–O32^{V}	130(14)
Intradimer hydrogen bonds					
O17–H171···O25	2.86(1)	H171···O25	2.14(4)	O17–H171–O25	152(3)
O27–H271···O16	2.83(1)	H271···O16	1.209(9)	O27–H271–O16	154(11)
O25–H251···O17	2.88(1)	H251···O17	2.2(1)	O25–H251–O17	127(8)

Symmetry code used to generate equivalent atoms: $^{I}x+1, -y, -z$; $^{II}x-1, y, z$; $^{III}-x=1, -y, -z+1$; $^{IV}-x+2, -y+1, -z$; $^{V}x, y, z+1$.

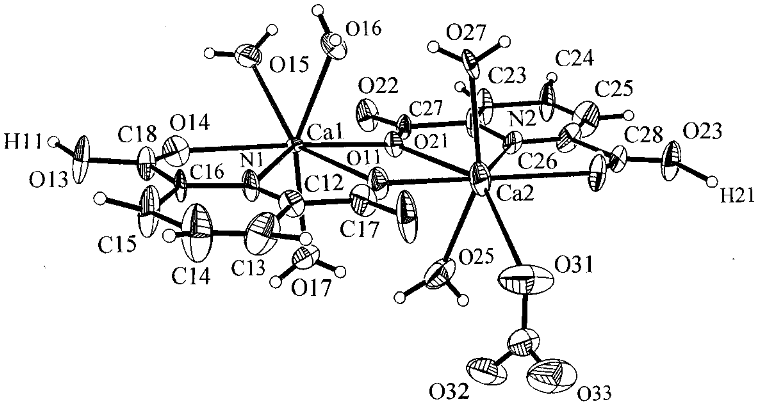

FIGURE 1 The view of $Ca_2(2,6\text{-PDDC})[H(2,6\text{-PDDC})](H_2O)_5NO_3$ dimer with atom numbering scheme. The non-hydrogen atoms are shown as 50% probability elipsoids.

these hydrogens bridge the dimers into molecular chains with a bridging pathway running *via* both carboxylate groups of the ligand molecule.

Two bridging pathways are thus operating in the title compound: the first in the molecular chain, which proceeds *via* the carboxylate ligands, the second – *via* the water oxygen atoms, links the chains into molecular sheets. Figure 2 shows a fragment of this molecular sheet.

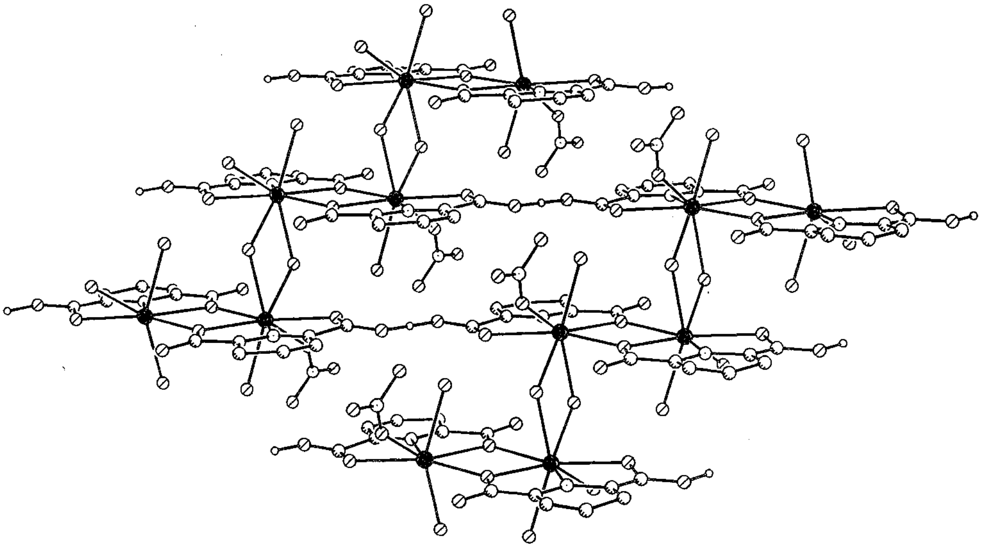

FIGURE 2 A fragment of the molecular sheet in the structure of $Ca_2(2,6\text{-}PDDC)[H(2,6\text{-}PDDC)](H_2O)_5NO_3$ showing the bridging modes *via* carboxylate hydrogen and water oxygen atoms. Only the bridging hydrogen atoms are shown. For clarity, the other are omitted.

In the case of short hydrogen bonds, the proton is located precisely in the center between two oxygen atoms forming a symmetrical hydrogen bond. However, since the potential energy curve for the position of a proton has a quite broad minimum and only a small amount of energy is required to shift it from the middle of the OHO bond, the following positions are also possible:

- the proton is located closer to one of the oxygen atoms resulting in an asymmetrical hydrogen bond;
- there is a statistical disorder in occupying by the proton the positions on either side of the center;
- the proton jumps between these positions giving rise to a dynamical disorder [7].

For example, such a short hydrogen bond [2.45 Å] has been recently observed in the crystal structure of potassium hydrogen dichloromaleate. An x-ray diffraction study carried out at room temperature located the carboxylate proton in the symmetry center between two carboxylate oxygens belonging to adjacent anions linking them into a polyanionic chain. However, a neutron diffraction study carried out at 30 and 293 K revealed that the proton is shifted from the center of symmetry by 0.15(1) Å, introducing in this way a local asymmetry in the overall centrosymmetric structure [8].

Hydrogen bonds of 2.62(1) Å link the bridging oxygen atoms O17 and O27 with carboxylate oxygen atoms O12 and O22 in adjacent dimers belonging to the same sheet. The sheets are held together by hydrogen bonds of 2.74(1) and 2.79(1) Å operating between the non-bridging water oxygen atoms O15 and O16 and the nitrate oxygen atoms O32 and O33 from the adjacent sheet. Hydrogen bonds of 2.83(1) and 2.88(1) Å operating inside a dimer are also observed, linking the bridging water oxygen atoms O17 and O27 with non-bridging water oxygen atoms O25 and O16, respectively.

The observed dimeric molecules in the title compound constitute the basic structural units in the crystal structures of "calcium dipicolinate trihydrate" [1] and the complex described [2]. The observed bridging system *via* water molecules in the title compound is the same as that detected previously in "calcium dipicolinate trihydrate." However, in the structure of the title compound one of the non-bridging water oxygen atoms is replaced by an oxygen atom donated by a nitrate group.

The crystals of both polymorphic modifications of the compound described [3] show different structural patterns. Bridging *via* the water oxygen atoms is broken. Instead, molecular ribbons are formed in which Ca(II) ions are bridged by oxygen atoms belonging to different carboxylate groups of the dipiocolinate ligand. Besides water oxygen atoms, each Ca(II) ion is coordinated by two oxygen atoms, both donated by a nitrate group. This, and the previous [3] study, show that the crystals of calcium dipicolinates exhibit a marked ability to accommodate ligands other than water molecules.

In the title compound the calcium carboxylate interaction modes, Ca(II) coordination scheme and the range of $Ca–O_{carboxylate}$ bond lengths agree well with those most frequently reported large number Ca(II) complexes with carboxylate ligands [9].

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