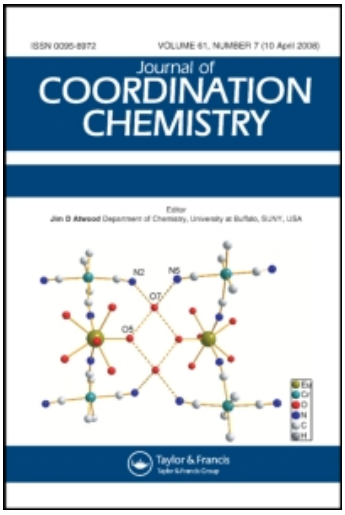

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The Crystal Structure of a Novel Calcium(II) Complex with Pyrazine-2,6-Dicarboxylate

Wojciech Starosta[a]; Halina Ptasiewicz-Bąk[a]; Janusz Leciejewicz[a]
[a] Institute of Nuclear Chemistry and Technology, ul.Dorodna 16, 03-195 Warszawa, Poland

To cite this Article Starosta, Wojciech , Ptasiewicz-Bąk, Halina and Leciejewicz, Janusz(2004) 'The Crystal Structure of a Novel Calcium(II) Complex with Pyrazine-2,6-Dicarboxylate', Journal of Coordination Chemistry, 57: 2, 167 — 173
To link to this Article: DOI: 10.1080/00958970410001666189
URL: http://dx.doi.org/10.1080/00958970410001666189

J. Coord. Chem., Vol. 57, No. 2, 20 January 2004, pp. 167–173

Taylor & Francis
Taylor & Francis Group

THE CRYSTAL STRUCTURE OF A NOVEL CALCIUM(II) COMPLEX WITH PYRAZINE-2,6-DICARBOXYLATE

WOJCIECH STAROSTA, HALINA PTASIEWICZ-BĄK and JANUSZ LECIEJEWICZ*

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

(Received 5 March 2003; Revised 8 August 2003; In final form 20 January 2004)

The structure of *catena*-{bis(aqua-μ-*O*)[di(aqua-*O*)bis(pyrazine-2,6-dicarboxylato-*O*,*N*-μ-*O*′)dicalcium(II)]}-di(pyrazine-2,6-dicarboxylic acid) hexahydrate consists of dimeric units composed of two calcium(II) ions, two ligand molecules and six water molecules. The calcium ions are bridged by two bidentate oxygen atoms, each donated by one carboxylate 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. Both calcium ions in a dimer are bridged to the Ca(II) ions in adjacent dimers by a pair of water molecules, forming infinite molecular ribbons. In addition, each Ca(II) ion is coordinated by two water molecules. The coordination polyhedron around the Ca(II) ion is a pentagonal bipyramid with two apices above and one apex below the equatorial plane. Six solvation water molecules and two pyrazine-2,6-dicarboxylic acid molecules per unit cell interact via a system of hydrogen bonds with the molecular ribbons.

Keywords: Pyrazine-2,6-dicarboxylic acid; Calcium(II) complexes; Molecular ribbons; X-ray diffraction

INTRODUCTION

Crystal-structure studies of calcium(II) coordination compounds with pyridine-2,6-dicarboxylate and pyridine-3,5-dicarboxylate ligands [1–4] revealed the existence of a number of phases with a common structural feature, namely, dimeric units composed of two Ca(II) ions bridged by two carboxylate oxygen atoms each donated by a different ligand molecule. The coordination around the metal ion was found to be completed by water oxygen atoms. The dimers occur either as single structural units [2,3] or, bridged by a pair of coordinating water oxygen atoms, forming polymeric molecular ribbons [1,4]. The latter molecular pattern has also been detected in the structures of two calcium(II) complexes with pyrazine-2,6-dicarboxylate and water ligands [5]. Recently, we obtained single crystals of a third calcium complex with the above ligands. The results of an X-ray diffraction study of its crystal structure are reported in this article.

*Corresponding author. Fax: +48-228-111-917. E-mail: jlec@orange.ichtj.waw.pl

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001666189

EXPERIMENTAL

Crystals of the title compound were found in the mother liquid after room-temperature evaporation of an aqueous solution containing calcium nitrate tetrahydrate and pyrazine-2,6-dicarboxylic acid dihydrate in the stoichiometric ratio 1 : 1. Two kinds of colorless single crystals were observed: flat rectangular plates (the title compound) and enlongated pillars. The latter have been previously detected when the title acid reacted with calcium carbonate [5]. The crystals of the title compound decompose slowly in air. The dimensions of the sample crystal used for collecting X-ray diffraction data are given in Table I.

X-ray reflections were measured at room temperature using a KUMA KM4 four-circle diffractometer operating in ω–2θ mode. Two standard reflections were monitored every 200 reflections. Since after four days their intensities were gradually reduced to 74.54% of their initial values, the maximum value of 2θ for data collection had to be limited to 44.00°. 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. Nonhydrogen atoms were located by Patterson synthesis using the SHELXLS program [6] and hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2

TABLE I Crystal data and structure refinement details for $[Ca_2(2,6\text{-}PZDC)_2(H_2O)_6]\cdot 2[H_2(2,6\text{-}PZDC)]\cdot 6H_2O$

Empirical formula	$C_{12}H_{18}N_4O_{14}Ca$
Formula weight	482.39
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å)	$a = 6.248(1)$
	$b = 9.382(2)$
	$c = 17.046(3)$
	$\alpha = 76.59(3)$
	$\beta = 80.21(3)$
	$\gamma = 87.42(3)$
V (Å)	957.80
Z	2
Calculated density ($g\,cm^{-3}$)	1.673
μ (Mo Kα) (mm^{-1})	0.41
$F(000)$	500.0
Crystal size (mm^3)	$0.2 \times 0.2 \times 0.4$
Max 2θ for data collection (°)	44.00
Index range	$-6 \le h \le 0$, $-9 \le k \le 9$, $-17 \le l \le 17$
No. of measured reflections	1706
No. of unique reflections with $F_o > 4\sigma(F_o)$	1377
R_{int}	0.0308
Method of structure solution	Patterson
Method of structure refinement	Full-matrix least squares on F^2
No. of parameters refined	353
Goodness-of-fit on F^2	1.081
Final $R1$ [$F_o > 4\sigma(F_o)$]	0.0380
Final $wR2$ index	0.1086
Largest diff. peak and hole ($e\,Å^{-3}$)	0.24 and −0.31
Weight parameters (A, B)	0.0657, 1.15
Mean shift/esd	0.006

by full-matrix least-squares methods 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: $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, 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 [7]. Final atomic coordinates and equivalent isotropic displacements are listed in Table II. Selected bond lengths and angles are collected in Table III.

TABLE II Atomic coordinates and equivalent isotropic displacements (Å^2) for $[Ca_2(2,6\text{-PZDC})_2(H_2O)_6] \cdot 2[H_2 2,6\text{-PZDC})] \cdot 6H_2O$

Atom	*x*	*y*	*z*	U_{eq}
Ca	0.2649(2)	0.3634(1)	0.4855(1)	0.0215(6)
N(1)	0.1692(6)	0.1799(4)	0.6191(3)	0.020(1)
C(2)	−0.0259(8)	0.1819(6)	0.6653(3)	0.023(1)
C(3)	−0.0906(9)	0.0693(6)	0.7323(4)	0.029(1)
N(2)	0.0437(7)	−0.0448(5)	0.7555(3)	0.036(1)
C(5)	0.2417(9)	−0.0424(7)	0.7088(4)	0.030(1)
C(6)	0.3034(8)	0.0686(6)	0.6404(3)	0.023(1)
C(7)	−0.1711(9)	0.3130(6)	0.6372(4)	0.024(1)
O(1)	−0.0960(5)	0.4059(4)	0.5742(2)	0.024(1)
O(2)	−0.3575(6)	0.3143(4)	0.6794(2)	0.033(1)
C(8)	0.5247(9)	0.0746(7)	0.5849(3)	0.026(1)
O(3)	0.5511(6)	0.1788(4)	0.5220(2)	0.029(1)
O(4)	0.6612(6)	−0.0224(4)	0.6068(2)	0.032(1)
O(5)	0.0039(7)	0.1966(5)	0.4585(3)	0.039(1)
O(6)	0.3551(7)	0.3178(5)	0.3460(3)	0.040(1)
O(7)	0.3930(6)	0.4887(5)	0.5808(3)	0.029(1)
N(11)	0.8806(8)	0.3121(7)	0.8677(4)	0.054(2)
C(12)	0.7238(1)	0.4123(6)	0.8522(1)	0.040(2)
C(13)	0.5296(9)	0.4114(6)	0.9043(3)	0.026(1)
N(12)	0.4849(7)	0.3096(5)	0.9753(3)	0.032(1)
C(15)	0.6417(9)	0.2102(7)	0.9909(4)	0.037(1)
C(16)	0.8337(9)	0.2126(8)	0.9372(5)	0.052(2)
C(17)	0.3549(9)	0.5214(7)	0.8808(4)	0.032(1)
O(11)	0.1963(7)	0.5261(5)	0.9399(3)	0.045(1)
O(12)	0.3690(7)	0.5971(5)	0.8113(3)	0.045(1)
C(18)	0.5917(11)	0.0938(8)	1.0690(4)	0.047(2)
O(13)	0.7398(9)	−0.0069(6)	1.0747(4)	0.084(2)
O(14)	0.4389(9)	0.0959(7)	1.1180(4)	0.104(3)
O(21)	0.0908(8)	0.5778(7)	0.6956(4)	0.051(1)
O(22)	0.9180(10)	0.7109(8)	0.8929(5)	0.086(2)
O(23)	0.6954(9)	0.7710(6)	0.1959(3)	0.050(1)
H(11)	0.114(10)	0.611(7)	0.924(4)	0.04(2)
H(13)	0.693(19)	−0.083(14)	1.126(8)	0.17(5)
H(51)	−0.131(12)	0.192(7)	0.476(4)	0.05(2)
H(52)	0.060(17)	0.101(11)	0.437(6)	0.13(4)
H(61)	0.363(10)	0.209(8)	0.351(4)	0.05(2)
H(62)	0.438(17)	0.357(11)	0.309(6)	0.12(4)
H(71)	0.460(11)	0.421(8)	0.616(4)	0.06(2)
H(72)	0.299(12)	0.526(7)	0.621(4)	0.05(2)
H(211)	0.020(18)	0.654(11)	0.668(6)	0.12(4)
H(212)	0.109(12)	0.611(8)	0.732(5)	0.06(3)
H(221)	0.939(12)	0.802(9)	0.855(5)	0.06(3)
H(222)	0.956(8)	0.773(6)	0.920(3)	0.00(1)
H(231)	0.785(17)	0.716(11)	0.197(6)	0.10(4)
H(232)	0.608(16)	0.712(11)	0.240(6)	0.11(4)

TABLE III Selected bond lengths (Å) and angles (°) in $[Ca_2(2,6\text{-PZDC})_2(H_2O)_6]\cdot 2H_2(2,6\text{-PZDC})]\cdot 6H_2O$

Calcium ion coordination			
Ca–O(11)	2.564(4)	Ca–O(1)–Ca^{I}	111.0(1)
Ca–O(1)^{I}	2.444(4)	O(1)–Ca–O(1)^{I}	69.0(1)
Ca–O(7)	2.464(4)	Ca–O(7)–Ca^{II}	111.7(1)
Ca–O(7)^{II}	2.547(4)	O(7)–Ca–O(7)^{II}	68.3(1)
Ca–O(3)	2.487(4)	O(3)–Ca–N(1)	64.4(1)
Ca–N(1)	2.514(4)	O(5)–Ca–O(3)	97.9(1)
Ca–O(5)	2.478(4)	O(5)–Ca–N(1)	75.5(1)
Ca–O(6)	2.480(5)	O(5)–Ca–O(1)	74.9(1)
		O(5)–Ca–O(1)^{I}	97.4(1)
		O(5)–Ca–O(6)	67.4(1)
		O(6)–Ca–O(7)^{II}	74.8(1)
		O(3)^{I}–Ca–O(7)	88.3(1)
Pyrazine-2,6-dicarboxylate ligand			
N(1)–C(2)	1.336(7)	C(6)–N(1)–C(2)	118.5(5)
C(2)–C(3)	1.381(8)	N(1)–C(2)–C(3)	121.1(5)
C(3)–N(2)	1.357(7)	C(2)–C(3)–N(2)	121.4(5)
N(2)–C(5)	1.351(7)	C(3)–N(2)–C(5)	116.2(5)
C(5)–C(6)	1.383(8)	N(2)–C(5)–C(6)	122.1(5)
C(6)–N(1)	1.333(7)	C(5)–C(6)–N(1)	120.6(5)
C(2)–C(7)	1.530(7)		
C(7)–O(1)	1.250(6)	O(1)–C(7)–O(2)	126.7(5)
C(7)–O(2)	1.262(7)		
C(6)–C(8)	1.532(8)		
C(8)–O(3)	1.265(7)	O(3)–C(8)–O(4)	126.8(5)
C(8)–O(4)	1.255(7)		
Pyrazine-2,6-dicarboxylic acid molecule			
N(11)–C(12)	1.343(8)	C(16)–N(11)–C(12)	114.8(5)
C(12)–C(13)	1.376(8)	N(11)–C(12)–C(13)	122.6(6)
C(13)–N(12)	1.352(7)	C(12)–C(13)–N(12)	121.9(5)
N(12)–C(15)	1.338(7)	C(13)–N(12)–C(15)	115.4(5)
C(15)–C(16)	1.378(9)	N(12)–C(15)–C(16)	121.4(6)
C(16)–N(11)	1.324(8)	C(15)–C(16)–N(11)	123.9(6)
C(13)–C(17)	1.508(8)		
C(17)–O(11)	1.295(7)	O(11)–C(17)–O(12)	125.3(5)
C(17)–O(12)	1.222(7)		
O(11)–H(11)	0.94(7)		
C(15)–C(18)	1.509(9)		
C(18)–O(13)	1.292(8)	O(13)–C(18)–O(14)	124.4(6)
C(18)–O(14)	1.159(8)		
O(13)–H(13)	1.0(1)		
Hydrogen bonds			
Coordinating water molecules			
D–H···A	D–A	H···A	D–H–A
O(5)–H(51)···O(3)^{V}	2.850(6)	2.01(7)	177(6)
O(5)–H(52)···O(4)^{VI}	2.833(6)	2.0(1)	137(10)
O(6)–H(61)···O(4)^{VI}	2.702(6)	1.73(7)	160(6)
O(6)–H(62)···O(12)^{II}	2.891(6)	2.2(1)	159(10)
O(7)–H(71)···O(2)^{IV}	2.706(5)	1.82(8)	168(7)
O(7)–H(72)···O(21)	2.731(7)	1.79(7)	171(6)
Interstitial acid molecule			
O(11)–H(11)···O(22)^{V}	2.496(8)	1.60(6)	159(6)
O(13)–H(13)···O(23)^{VIII}	2.541(8)	1.6(1)	160(11)
Solvation water molecules			
O(21)–H(211)···O(6)^{I}	3.054(7)	2.4(1)	130(9)
O(21)–H(212)···O(12)	2.882(8)	2.27(8)	137(10)
O(22)–H(221)···N(2)^{VII}	2.899(8)	1.99(8)	162(7)
O(22)–H(222)···O(11)^{IV}	2.496(7)	1.7(1)	129(10)
O(23)–H(231)···N(11)^{III}	2.843(8)	2.2(1)	138(9)
O(23)–H(232)···O(2)^{I}	2.7535(7)	1.9(1)	149(9)

Symmetry code: $^{I}-x, -y+1, -z+1$; $^{II}-x+1, -y+1, -z+1$; $^{III}-x+2, -y+1, -z+1$; $^{IV}x+1, y, z$; $^{V}x-1, y, z$; $^{VI}-x+1, -y, -z+1$; $^{VII}x+1, y+1, z$; $^{VIII}x, y-1, z+1$.

DISCUSSION

The structure of the title compound contains dimeric units consisting of two calcium(II) ions, two ligand molecules and six water molecules. A dimer with the atom numbering is shown in Fig. 1. The calcium ions are bridged by two oxygen atoms each donated by a different ligand molecule [O(1) and $O(1)^{I}$]. The bridging oxygen atom belongs to one carboxylate group of the ligand. The second oxygen atom of this group does not coordinate the metal ion. Apart from the two bridging carboxylate oxygen atoms, the calcium ion is coordinated by an oxygen atom donated by the second carboxylate oxygen atom of the ligand molecule [O(3)], the hetero ring nitrogen atom [N(1)], two water oxygen atoms [O(5) and O(6)] and two water oxygen atoms [O(7) and $O(7)^{II}$]. The latter bridge links the dimeric units into molecular ribbons. Figure 2 shows a fragment of a ribbon. The atoms of the pyrazine rings in a dimer are coplanar with shifts from the mean plane in the range +0.076(1) [N(2)] to −0.033(1) Å [the N(1) atom]. The bridging bidentate carboxylate oxygen atom O(1) deviates by −0.093(1) Å, while the other coordinating carboxylate oxygen atom O(3) is shifted by −0.015(1) Å. The Ca ion deviates from the mean plane by +0.185(1) Å.

The coordination number of a Ca(II) ion in the title compound is eight. The relevant bond distances and angles are listed in Table III. The coordination polyhedron can be visualized as a pentagonal bipyramid with two apices on one side of the equatorial plane and one apex on the other side. The strongly distorted equatorial plane is formed by the Ca, N(1), O(1), $O(1)^{I}$, O(3) and $O(7)^{II}$ atoms with the shifts from the average plane ranging from −0.450(1) [$O(7)^{II}$] to +0.374(1) Å (Ca). The minimum shift of −0.181(1) Å is shown by the coordinating N(1) atom. The O(5) and O(6) water oxygen atoms form the two apices, while the single apex is occupied by the bridging

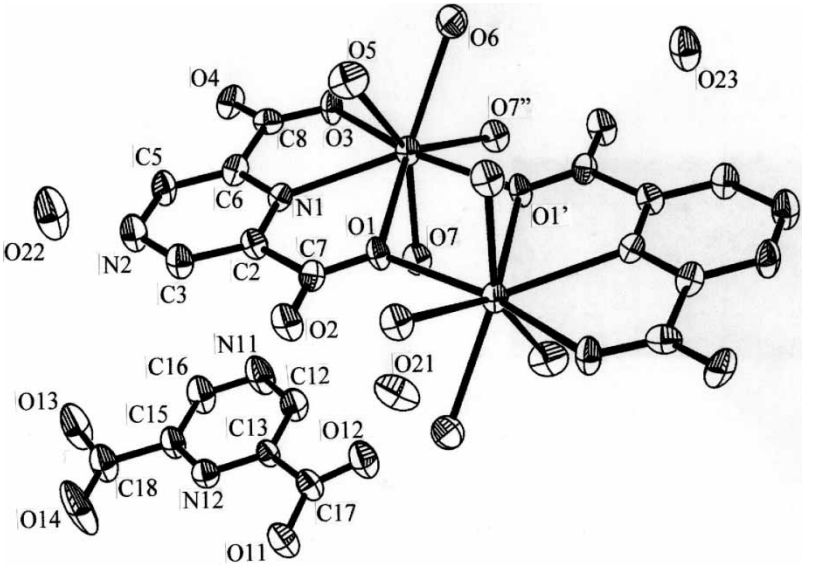

FIGURE 1 The dimeric structural unit, an interstitial acid and solvation water molecules in the structure of $[Ca_2(2,6\text{-PZDC})_2(H_2O)_6]\cdot 2[H_2(2,6\text{-PZDC})]\cdot 6H_2O$ with atom numbering scheme. The nonhydrogen atoms are shown as 50% probability ellipsoids. For clarity, hydrogen atoms are omitted. O(21), O(22) and O(23) denote the oxygen atoms of solvation water molecules.

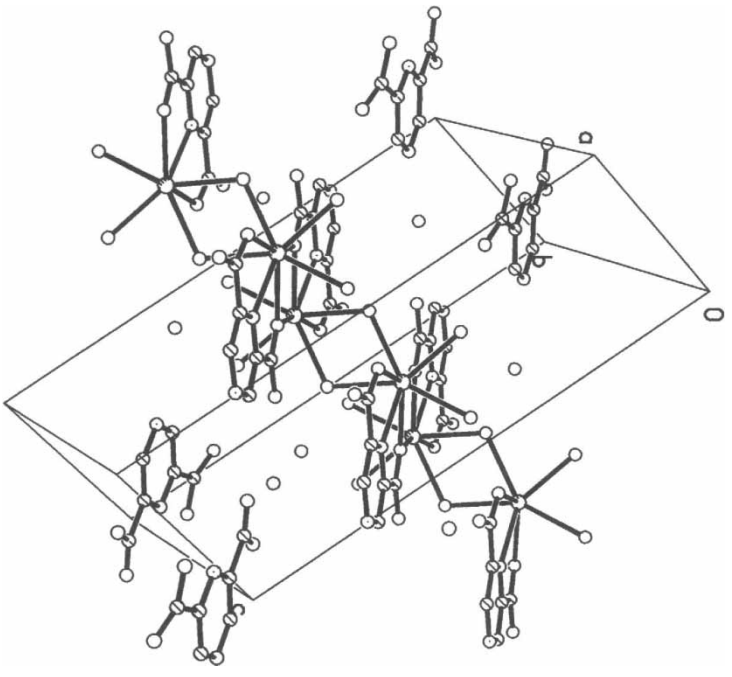

FIGURE 2 The alignment of a molecular ribbon with respect to the unit cell in the structure of $[Ca_2(2,6\text{-}PZDC)_2(H_2O)_6]\cdot 2[H_2(2,6\text{-}PZDC)]\cdot 6H_2O$.

water oxygen atom O(7). Ordered distribution of ligand acid molecules has been detected in the space between the ribbons. The atoms which form the pyrazine ring of the acid molecule are coplanar: the shifts fall between +0.036(1) Å [C(17)] and −0.083(1) Å [C(12)]. On the other hand, the carboxylate oxygen atoms deviate strongly from the mean plane: −0.168(1) Å [O(11)], +0.274(1) Å [O(12)], +0.182(1) Å [O(13)] and only −0.051(1) Å [O(14)]. The observed bond lengths and angles within the ligand molecule and the interstitial acid molecule do not differ from those observed in the structures of pyrazine-2,6-dicarboxylic acid dihydrate [8].

The molecular ribbons interact by a network of hydrogen bonds in which all coordinating water molecules act as donors. The acceptors are the carboxylate oxygen atoms in adjacent ribbons, the carboxylate oxygen atom of the interstitial acid molecule [$O(12)^{II}$] and the solvation water molecule [O(21)]. The corresponding D–H···A distances range from 2.702(6) to 2.891(6) Å. The solvation water oxygen atoms also participate in this network as donors in bonds to carboxylate oxygen and hetero-ring nitrogen atoms of the ligand and interstitial acid molecules, while the interstitial acid hydroxyl groups form fairly short hydrogen bonds of 2.496(8) and 2.541(8) Å to two solvation water oxygen atoms (see Table III).

The basic structural motif observed in the title compound – molecular ribbons composed of dimeric assemblies bridged by water oxygen atoms – has been recently detected in the structures of two calcium complexes with pyrazine-2,6-dicarboxylate and water ligands [5]. The first complex does not contain solvation water molecules, the second contains four per unit cell, while the unit cell of the third complex – the title compound – apart from six solvation water also contains two ligand acid molecules. This effect is accompanied by an increase of unit cell volume from 484.40 $Å^3$

in the first complex, via 532.10 $Å^3$ observed in the second, to 957.80 $Å^3$ determined in the title compound.

Discrete ligand acid molecules have also been found to be accommodated in the structure of a Ca(II) complex with pyridine-2,6-dicarboxylate and water ligands [3]. Since the latter ligand has the same shape and dimensions as the title ligand, one may connect this feature with the geometrical shape of the ligand molecule.

The Ca(II) coordination mode and the range of calcium–carboxylate oxygen and calcium–water oxygen atom bond distances in the title compound agree fairly well with those most commonly observed in the structures of a large number of Ca(II) complexes with carboxylate ligands [9].

Supplementary Data

Listings of the observed and calculated structure factors and anisotropic thermal parameters can be requested from the authors. Detailed data on the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre under the code number CCDC 217294.

References

[1] G. Strahs and R.E. Dickerson, *Acta Crystallogr.* **B24**, 571 (1968).
[2] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **55**, 1 (2002).
[3] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **55**, 469 (2002).
[4] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **55**, 1147 (2002).
[5] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **56**, 677 (2003).
[6] G.M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1990).
[7] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement (University of Göttingen, Göttingen, Germany, 1997).
[8] H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **56**, 173 (2003).
[9] H. Einspahr and C.E. Bugg, *Acta Crystallogr.* **B37**, 1044 (1981).