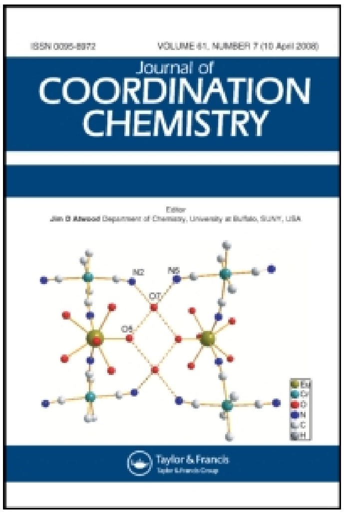

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THE CRYSTAL STRUCTURES OF TWO CALCIUM(II) COMPLEXES WITH PYRAZINE-2,6-DICARBOXYLATE AND WATER LIGANDS

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The structure of *catena*-{bis[(μ-aqua)(diaqua)(pyrazine-2,6-dicarboxylato-O,N-μ-O′)](calcium(II)} 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 carboxylic group of the ligand. The Ca(II) ion is also coordinated by one oxygen atom of the second carboxylate group and the heteroring nitrogen atom belonging to the same ligand molecule. 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 three water molecules; one of them is used for bridging the adjacent dimer. The coordination polyhedron around the Ca(II) ion is a pentagonal bipyramid with two apices above and one apex below the equatorial plane. The same molecular pattern is observed in the structure of *catena*-{bis[(μ-aqua) (diaqua)(pyrazine-2,6-dicarboxylato-O,N-μ-O′)](calcium(II)} dihydrate which, in addition, contains two solvation water molecules per unit cell. In both compounds the molecular ribbons are held together by extended systems of hydrogen bonds.

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

INTRODUCTION

Structural data collected for calcium(II) complexes with pyridine-3,5-dicarboxylate and pyridine-2,6-dicarboxylate ligands indicate a tendency of the Ca(II) ion to form a number of crystal phases exhibiting molecular patterns containing dimeric units [1–4]. Since another ligand with the same geometry is represented by pyrazine-2,6-dicarboxylic (2,6-PZDC) molecule, it seemed to be of interest to investigate whether the structure of the Ca(II) complex with this ligand also contains dimeric units. The results of this study are reported below.

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EXPERIMENTAL

Both title compounds were obtained by adding an excess of calcium carbonate to 100 mL of boiling aqueous solution containing 1.0 mmol of pyrazine-2,6-dicarboxylic acid dihydrate. The mixture was stirred and refluxed for one hour; then, the undissolved calcium carbonate was filtered off. After few days two kinds of colorless, well-formed single crystals were found in the mother liquid: elongated pillars (title compound 1) and needles (title compound 2). The dimensions of the crystals used for x-ray diffraction data collection 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. 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 [5] and hydrogen atoms then found

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

Empirical formula	$C_6H_7N_2O_7Ca$	$C_6H_{10}N_2O_8Ca$
Formula weight	260.23	278.23
Temperature	293 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	$a = 5.937(1)$ Å	$a = 5.930(1)$ Å
	$b = 8.566(2)$ Å	$b = 8.949(2)$ Å
	$c = 9.777(2)$ Å	$c = 10.386(2)$ Å
	$\alpha = 88.32(3)°$	$\alpha = 88.93(3)°$
	$\beta = 89.94(3)°$	$\beta = 80.34(3)°$
	$\gamma = 77.07(3)°$	$\gamma = 78.39(3)°$
	$V = 484.40$ Å^3	$V = 532.10$ Å^3
Z	2	2
Calculated density	1.784 gcm^{-3}	1.730 gcm^{-3}
μ (MoKα)	0.67 mm^{-1}	0.63 mm^{-1}
$F(000)$	268	288
Crystal size	$0.2 \times 0.2 \times 0.4$ mm^3	$0.2 \times 0.1 \times 0.3$ mm^3
Max 2θ for data collection (deg.)	60.19	60.14
Index range	$-8 \le h \le 0$	$-8 \le h \le 0$
	$-12 \le k \le 11$	$-12 \le k \le 12$
	$-13 \le l \le 13$	$-14 \le l \le 14$
No. of measured reflections	2337	2117
No. of unique reflections with $F_o > 4\sigma(F_o)$	1847	1452
R_{int}	0.0186	0.0255
Method of structure solution	direct method	
Method of structure refinement	full-matrix least squares on F^2	
No. of parameters refined	177	190
Goodness-of-fit on F^2	1.083	1.027
Final $R1$ $[F_o > 4\sigma(F_o)]$	0.0317	0.0377
Final $wR2$ index	0.0957	0.1066
Absorption correction	Ψ-scan	
Min. and max. transmission factors	0.689, 0.836	0.652, 0.800
Largest diff. Peak and hole	0.38 e A^3 and -0.38 e Å^3	0.55 e A^3 and -0.34 e Å^3
Weight parameters (A, B)	0.0639, 0.09	0.0676, 0.00
Mean shift/esd	0.001	0.005

TABLE II Selected bond lengths (Å) and angles (deg.) for [Ca_2(2,6-PZDC)$_2$(H_2O)$_6$] (1) and [Ca_2(2,6-PZDC)$_2$(H_2O)$_6$]·H_2O (2)

	1	*2*		*1*	*2*
Ca–O3	2.365(2)	2.613(2)	Ca–O3–Ca$^{\mathrm{I}}$	106.9(1)	108.0(1)
Ca–O3$^{\mathrm{I}}$	2.582(2)	2.391(3)	O3–Ca–O3$^{\mathrm{I}}$	73.1(1)	72.0(1)
Ca–O7	2.478(2)	2.458(3)	Ca–O7–Ca$^{\mathrm{II}}$	112.1(1)	111.3(1)
Ca–O7$^{\mathrm{II}}$	2.570(2)	2.534(3)	O7–Ca–07$^{\mathrm{II}}$	67.9(1)	68.7(1)
Ca–O1	2.407(2)	2.434(3)	O1–Ca–N1	64.2(1)	64.1(1)
Ca–N1	2.517(2)	2.520(3)	O5–Ca–O1	107.1(1)	105.9(1)
Ca–O5	2.406(2)	2.380(3)	O5–Ca–N1	87.6(1)	83.7(1)
Ca–O6	2.475(2)	2.431(3)	O5–Ca–O3	86.6(1)	75.1(1)
			O5–Ca–O3$^{\mathrm{I}}$	72.4(1)	88.3(1)
			O5–Ca–O6	69.1(1)	70.3(1)
			O6–Ca–O7$^{\mathrm{II}}$	73.6(1)	72.5(1)
			O3$^{\mathrm{I}}$–Ca–O7	74.9(1)	84.7(1)

Hydrogen bonds (*title compound 1*):

D–H···A	D–A	H···A	D–H–A
O5–H51···O1$^{\mathrm{VI}}$	2.690(3)	1.92(4)	163(3)
O5–H52···O1$^{\mathrm{III}}$	2.981(3)	2.19(3)	155(3)
O6–H61···N2$^{\mathrm{V}}$	2.871(3)	2.04(4)	177(3)
O6–H62···O2$^{\mathrm{IV}}$	2.846(3)	1.99(4)	164(3)
O7–H71···O5$^{\mathrm{I}}$	2.911(3)	2.36(6)	134(4)
O7–H72···O4$^{\mathrm{II}}$	2.651(3)	1.99(5)	145(5)

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

Hydrogen bonds (*title compound 2*)

D–H···A	D–A	H···A	D–H–A
O5–H51···O1$^{\mathrm{VI}}$	2.701(3)	1.89(4)	170(3)
O5–H52···O10$^{\mathrm{II}}$	2.887(3)	2.13(3)	156(3)
O6–H61···O10$^{\mathrm{III}}$	2.754(3)	1.95(4)	165(3)
O6–H62···O1$^{\mathrm{VIII}}$	3.071(3)	2.36(4)	156(4)
O7–H71···O10$^{\mathrm{I}}$	3.120(3)	2.47(4)	140(3)
O7–H72···O4$^{\mathrm{V}}$	2.611(3)	1.98(6)	151(4)
O10–H11···N2$^{\mathrm{VII}}$	2.819(3)	2.11(5)	167(5)
O10–H12···O2$^{\mathrm{IV}}$	2.718(3)	1.66(5)	149(5)

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

by successive Fourier syntheses. Final refinement of F^2 by full-matrix least squares 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 refined parameters listed in Table I. Calculations were carried out using the SHELXL97 program [6]. Selected bond lengths and angles are listed in Table II. Listings of the observed and calculated structure factors and anisotropic thermal parameters can be requested from the authors.

DISCUSSION

The structures of both title compounds contain dimeric assemblies 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–O3; Ca–O3^{I}). This oxygen atom belongs to one of the carboxylic groups of the ligand and acts as a bridging ligand. The second oxygen atom of this group is not coordinated to the metal ion. Apart from the two bridging carboxylate oxygen atoms, the calcium ion is coordinated by an oxygen atom donated by the second carboxylic group of the ligand molecule (Ca–O1), the hetero-ring nitrogen atom (Ca–N) and three water molecules. Figure 1 shows a molecular dimer with atom numbering scheme valid for both title compounds. One of the water oxygen atoms (O7) bridges the Ca(II) ion in the adjacent dimer jointly with a water oxygen atom (07^{I}) donated from the coordination polyhedron of the latter metal ion. In this way, the dimers are catenated by pairs of water oxygen atoms (see, Fig. 2). The Ca(II) ions and the atoms of the 2,6-PZDC ligand molecules in a dimer are coplanar with the shifts from the mean plane in the range from −0.306(1) Å the Ca ion to +0.223(1) Å the C5 atom in the case of title compound I and from +0.179(1)Å the Ca atom to −0.149(1) Å the O3 atom of title compound 2. The bridging bidentate carboxylate oxygen atoms O1 are shifted by −0.023(1) Å in compound 1 and by +0.026(1) Å in compound 2; the O3 atoms: −0.035(1) Å in compound 1 and −0.149(1) Å in compound 2.

The coordination number of a Ca(II) ion in both title compounds is eight. The respective coordination polyhedron can be visualized as pentagonal bipyramid with two apices on one side of the equatorial plane and one apex on the other side. The equatorial plane is formed by the Ca, O3^{I}, O5, O6, O7 and O7^{II} atoms. In the structure of title compound 1, the shifts from the average equatorial plane range from −0.297(1) Å (the 07^{II} atom) to +0.290(1) Å (the Ca atom). In the case of title compound 2, the equatorial plane is even more distorted, since the shifts range from +0.371(1) Å (the O7 atom) to −0.314(1) Å (the O7^{II} atom). In both compounds, the O1 and N1 atoms constitute the two apices, while the single apex is occupied by the bridging carboxylate atom O3. Table II lists the respective bond lengths and angles.

The catenated molecular dimers in title compound 1 are held together by a network of hydrogen bonds donated by the coordinating water molecules. The acceptors are the carboxylate oxygen atoms, the hetero-ring nitrogen atom (N2) and the coordinating

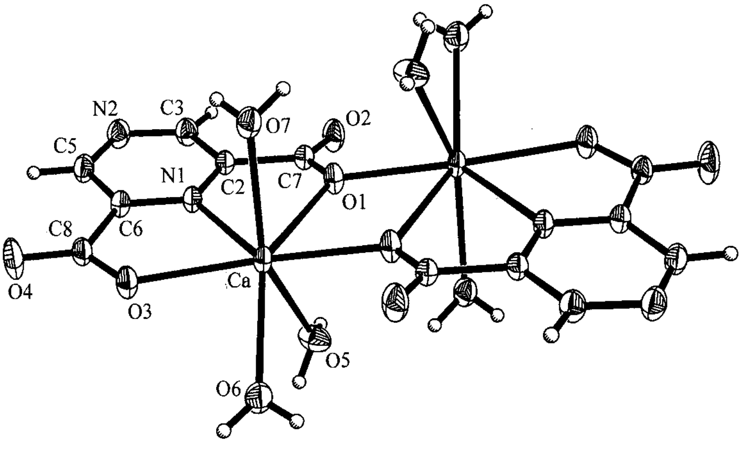

FIGURE 1 A structural unit $Ca_2(2,6\text{-PZDC})_2(H_2O)_6$ with atom numbering scheme. The non-hydrogen atoms are shown as 50% probability ellipsoids.

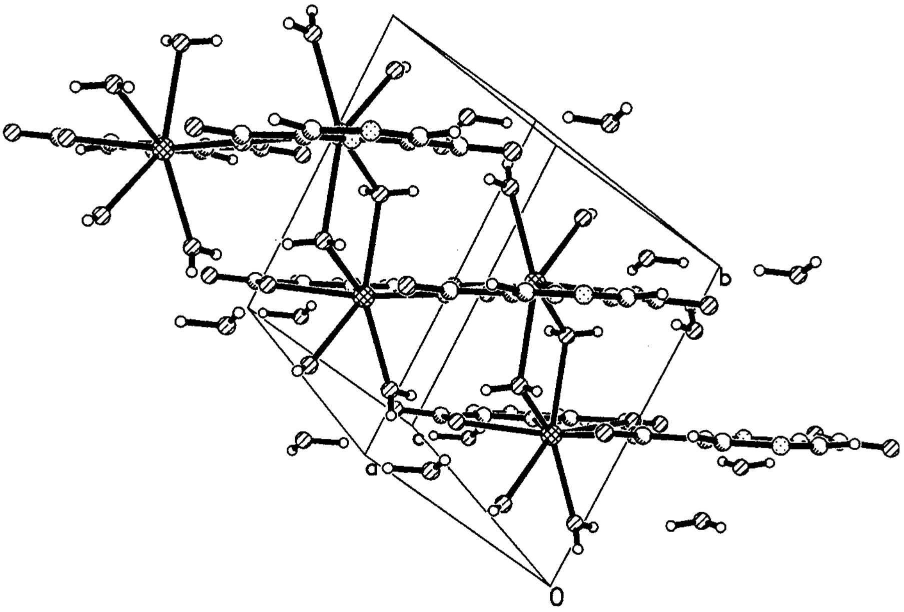

FIGURE 2 The alignment of catenated molecular dimers in the structure of $[Ca_2(2,6\text{-}PZDC)_2(H_2O)_6 \cdot 2H_2O$.

water oxygen atom (O5), all belonging to adjacent dimmers. In the structure of title compound 2 the coordinating water molecules act as donors (and acceptors) in the network of hydrogen bonds. In addition, the oxygen atom O10 of the solvation water molecule acts as a donor in a hydrogen bond to the unbonded hetero-ring nitrogen atom N2 and carboxylate oxygen atom in different neighboring dimers. The hydrogen bond lengths are listed in detail in Table II. The accommodation of two solvation water molecules per unit cell leads to small variation of lattice parameters and the enlargement of its unit cell volume from 484.40 $Å^3$ (compound 1) to 532.10 $Å^3$ (compound 2).

Molecular units in the form of catenated dimers bridged by pairs of water molecules have been earlier detected in two structures of calcium(II) complexes: with pyridine-2,6-dicarboxylic (2,6-PDDC) and water ligands [1] and with 2,6-PDDC, water and nitrate ligands [4]. The same molecular pattern as in the complex reported in [1] has been discovered recently in the structure of a strontium(II) complex with 2,6-PZDC and water ligands [7]. Discrete molecular dimers have been observed in the structures of a Ca(II) complex with the 3,5-PDDC and water ligands [2] and a complex with the 2,6-PDDC and water ligands [3]. All these ligands have the same shape and dimensions; all of them contribute the N, O bonding moiety to coordinate the metal ion. Thus, the inclination to form dimeric assemblies may be influenced by the geometry of the ligand molecule.

References

[1] G. Strahs and R.E. Dickerson, *Acta Cryst.* **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] G.M. Sheldrick, *Acta Cryst.*, **A46,** 467 (1990).
[6] G.M. Sheldrick, Program for crystal structure refinement. University of Göttingen, (1997).
[7] H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **56,** 223 (2003).