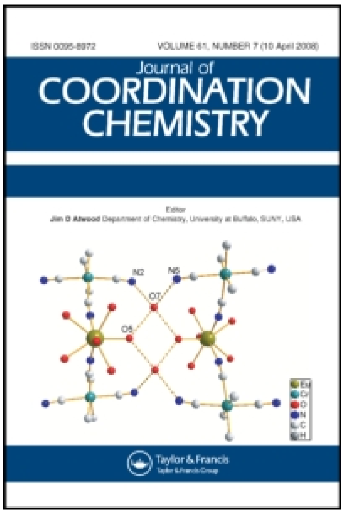

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Catenated polymeric molecular patterns in structures of two calcium(II) complexes with pyridine-2,3-dicarboxylate (quinolinic) and water ligands

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Catenated polymeric molecular patterns in structures of two calcium(II) complexes with pyridine-2,3-dicarboxylate (quinolinic) and water ligands

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The structure of triclinic *catena*-tetraquo(μ-pyridine-2,3-dicarboxylato-*N*,*O*; *O*′)calcium(II) is composed of two symmetry independent Ca(II) ions and two independent ligand molecules. Each Ca(II) is coordinated by a N,O-bonding moiety of a ligand, four water oxygens, and a carboxylate oxygen donated by an adjacent bridging ligand. The resulting molecular ribbons are propagating in the [010] crystal direction. Both Ca(II) ions are eight coordinate forming a capped pentagonal bipyramidal with strongly distorted pentagonal equatorial planes. Hydrogen bonds between carboxylate oxygens and coordinated waters are responsible for the stability of the structure. The orthorhombic structure of *catena*-trisaquo[(μ-2, 3-dicarboxypyridin-1-ium-*O*,*O*′; *O*″) (*H* pyridine-2,3-dicarboxylato-*N*,*O*)]calcium(II) is composed of molecular ribbons in which the bridging of Ca(II) ions occurs through a ligand using one bidentate carboxylate. The other carboxylate of this ligand donates only one O atom to Ca(II), the second remaining inactive. A proton is attached to the hetero-nitrogen. Each Ca(II) is also chelated by a N,O-bonding moiety of a second ligand, which does not bridge and its second carboxylate remains protonated. Three water oxygen atoms complete the coordination around the Ca(II) ion to eight. The resulting coordination polyhedron is a capped pentagonal bipyramid with a strongly distorted equatorial plane. Hydrogen bonds in which coordinated waters act as donors are responsible for the stability of the structure.

Keywords: calcium(II) complex; quinolinic ligand; crystal structure

1. Introduction

Crystal chemistry of Ca(II) coordination compounds with organic carboxylate ligands attracts considerable interest due to the role played by this element in living organisms [1, 2]. We started studies to determine the crystal structures of Ca(II) complexes with pyridine dicarboxylate ligands [3–8]. The majority of crystal structures exhibit polymeric molecular patterns in which metal ions are bridged by carboxylate oxygens, and in some structures by coordinated water. Catenated polymeric structures have been reported for a Ca(II) complex with pyridine-3,4-dicarboxylate and water [3], two complexes with pyridine-3,5-dicarboxylate and water [4, 5] and four complexes with pyridine-2,6-dicarboxylate and water [6–8]. The structures of two other complexes have been found to be composed of dimeric molecules [9, 10]. In all the complexes, Ca(II)

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ions show coordination numbers of seven or eight and a variety of bridging modes confirming the well-known bonding flexibility of this ion [2]. Continuing our studies of the structural chemistry of Ca(II) coordination compounds with azine carboxylate ligands, we have obtained two complexes with pyridine-2,3-dicarboxylate and water, grown single crystals and determined their crystal structures by X-ray diffraction. The results are reported in this article.

2. Experimental

Compound I (code name CAQUIN 1) was obtained by adding calcium carbonate to 50 mL of aqueous solution containing 1 mmol of pyridine-2,3-dicarboxylic acid (ALDRICH). The mixture was boiled for 2 h, then cooled to RT and the excess carbonate was filtered off. After evaporation to dryness during a couple of days, long colorless needles were found on the bottom of the crystallization pot. They were washed with cold methanol and dried in the air. A sample crystal was cleaved to proper dimensions and used for X-ray data collection.

Compound II (code name CAQUIN 2) was prepared by mixing 30 mL of hot aqueous solutions, one containing 2 mmols of pyridine-2,3-dicarboxylic acid (ALDRICH), the other – 1 mmol of Ca(II) acetate tetrahydrate. The mixture was boiled with stirring for 2 h and then cooled slowly to RT. After a few days, well-shaped rectangular colorless blocks were found in the mother liquid; one was taken for X-ray data collection.

X-ray diffraction data were collected 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 SDs were obtained by least-squares fit to 25 reflections in the 2θ range from 15° to 30°. Reflections were processed using profile analysis and corrected for Lorentz and polarization effects. Absorption corrections were applied in the analytical form [11]. Non-hydrogen atoms were located by direct methods. The positions of H atoms and their isotropic temperature factors were calculated using AFIX instruction. Final refinement on F^2 by full-matrix least-squares method was performed on both structures using positional parameters and anisotropic vibrational parameters of all non-H atoms and constrained values for H atoms [12]. Weighting scheme was used in the form: $w = 1/[\sigma^2(F^2{}_o) + (A^*P)^2 + B^*P]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. A, B are the parameters listed in table 1 with other data collection and refinement parameters.

3. Discussion

The asymmetric unit cell of CAQUIN 1 contains two symmetry-independent structural units, each composed of a Ca(II) coordinated by a ligand *via* its N,O-bonding moiety, four water oxygen, and a carboxylate oxygen donated by an adjacent structural unit. In this way, the structural units form molecular ribbons propagating in the [010] crystal direction bridged by O atoms donated by the second carboxylate groups of the adjacent ligands. Figure 1 shows the two symmetry-independent structural

Table 1. Crystal data and structure refinement details.

Identification code	CAQUIN 1	CAQUIN 2
Empirical formula	$C_7H_{11}N_1O_8Ca_1$	$C_{14}H_{14}N_2O_{11}Ca_1$
Formula weight	277.24	426.35
Temperature (K)	293(2)	
Wavelength (Å)	0.71073	
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1nb$
Unit cell dimensions (Å, °)		
a	7.884(2)	6.637(1)
b	10.192(3)	8.220(2)
c	13.776(3)	30.123(6)
α	80.41(3)	90
β	87.67(3)	90
γ	88.43(3)	90
V (Å^3)	1087.18	1643.34
Z	4	4
Calculated density (g cm^{-3})	1.694	1.719
μ (Mo-Kα) (mm^{-1})	0.61	0.45
F(000)	576.0	876.0
Crystal size (mm^3)	$0.076 \times 0.114 \times 0.382$	$0.097 \times 0.116 \times 0.252$
Max 2θ for data collection	56.23°	57.87°
Index range	$0 \leq h \leq 9$	$0 \leq h \leq 9$
	$-13 \leq k \leq 12$	$-1 \leq k \leq 11$
	$-18 \leq l \leq 16$	$0 \leq l \leq 39$
No. of measured reflections	4624	2218
No. of unique reflections with $F_o > 4\sigma(F_o)$	2515	1399
R(int)	0.0321	0.1352
Absorption correction	Analytical [11]	
Transmission factors	0.92536, 0.96409	0.94736, 0.96540
Method of structure solution	Direct method	
Method of structure refinement	Full-matrix least squares on F^2	
No. of parameters refined	339	309
Goodness-of-fit on F^2	0.960	1.078
Final R1 [$F_o > 4\sigma(F_o)$]	0.0492	0.0582
Final wR2 index	0.1631	0.1946
Largest diff. peak and hole (e Å^{-3})	0.55, −0.76	0.48, −0.52
Weight parameters (A, B)	0.1138, 0.00	0.0934, 3.81
Mean shift/esd	0.00	0.00

units with atom labels; figure 2, a fragment of a ribbon and its alignment in the unit cell. Pyridine rings of both ligand molecules are planar: r.m.s. is 0.0065(1) Å in the case of the ligand coordinated to Ca1 and 0.0081(1) Å for the ligand coordinated to Ca2. Carboxylate groups make the following dihedral angles with the pyridine rings: (C17/O11/O12) – 9.4(1)°, (C18/O13/O14) – 91.1(1)° and (C27/O21/O22) – 6.4(1)°, (C28/O23/O24) – 82.9(1)°. The observed bond distances and angles within the ligand does not differ from those reported for the parent acid [13]. The coordination geometry of both Ca(II) ions is capped pentagonal bipyramidal with strongly distorted pentagonal equatorial planes, bridging carboxylate O atoms and water O atoms forming the apices of the bipyramids. For Ca1 coordination polyhedron, the deviations from the mean equatorial plane [r.m.s. 0.2340(1)] range from −0.3691(1) for O11 to +0.4181(1) for O1, while for the coordination polyhedron around the Ca2 the relevant parameters are: r.m.s. 0.2285(1), maximum and minimum deviations from the mean equatorial plane +0.3082(1) for O5 and −0.1375(1) for O7. Table 2 lists the respective bond distances and angles, which fall in the range common for Ca(II)

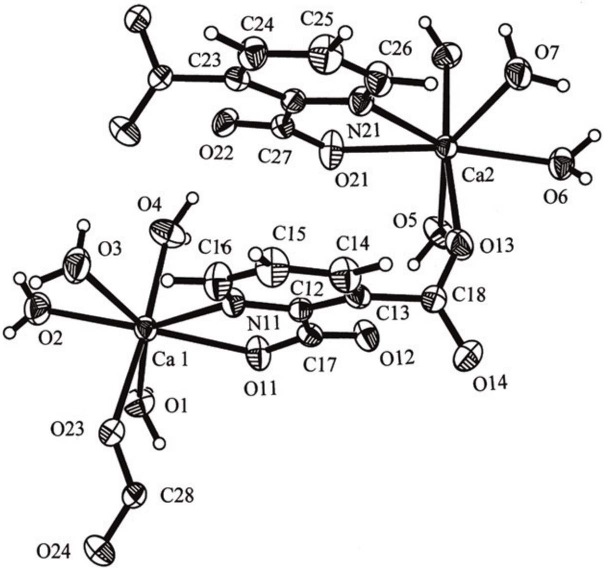

Figure 1. Molecular unit constituting the structure of *catena*-tetraquo(μ-pyridine-2,3-dicarboxylato-*N*,*O*; *O*′)calcium(II) with atom labeling.

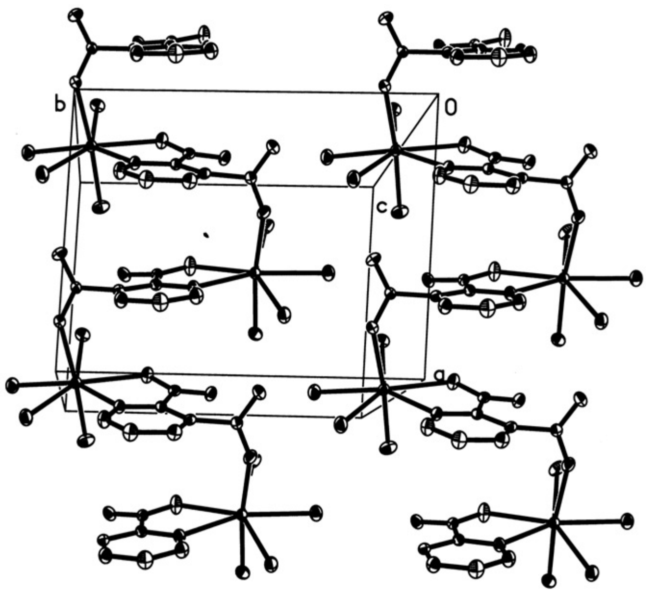

Figure 2. The alignment of a molecular ribbon in the unit cell of *catena*-tetraquo(μ-pyridine-2,3-dicarboxylato-*N*,*O*; *O*′)calcium(II).

carboxylate complexes [2]. Coordination number seven with bipyramidal geometry has been only discovered in complexes with pyridine-3,5-dicarboxylate and water ligands [4, 5], the other complexes with pyridine dicarboxylate ligands show coordination number eight.

Table 2. Selected bond distances and angles (Å, °) around Ca(II) ions in the structure of CAQUIN 1 complex.

Ca1 ion			
Ca1–N11	2.539(3)	O11–Ca1–N11	64.9(1)
Ca1–O11	2.396(3)	N11–Ca1–O3	77.9(1)
Ca1–O1	2.424(3)	O1–Ca1–O2	72.0(1)
Ca1–O2	2.548(3)	O2–Ca1–O3	74.3(1)
Ca1–O3	2.359(3)	O3–Ca1–O11	141.5(1)
Ca1–O23	2.320(3)	O23–Ca1–O4	173.1(1)
Ca1–O4	2.350(3)		
Ca2 ion			
Ca2–N21	2.615(3)	O21–Ca2–N21	63.7(1)
Ca2–O21	2.377(3)	N21–Ca2–O5	133.9(1)
Ca2–O5	2.427(3)	O5–Ca2–O6	74.8(1)
Ca2–O6	2.473(3)	O6–Ca2–O7	73.2(1)
Ca2–O7	2.389(4)	O7–Ca2–N21	75.3(1)
Ca2–O13	2.294(3)	O13–Ca2–O8	172.4(1)
Ca2–O8	2.406(4)		

Table 3. Geometrical parameters (Å, °) of H bonds in the structure of CAQUIN 1.

	D–H	H···A	D–H···A	D–H–A
O1–H12···O22^{a}	0.82	1.87	2.684(4)	169.1
O1–H12···O6^{f}	0.825(15)	2.16(3)	2.917(4)	152(6)
O2–H21···O8^{d}	0.820(15)	2.122(17)	2.941(5)	177(6)
O3–H31···O14^{h}	0.820(16)	1.99(2)	2.804(5)	170(6)
O3–H32···O24^{c}	0.82	1.97	2.717(5)	150.7
O4–H41···O2^{h}	0.82	2.07	2.845(5)	157.2
O4–H42···O22	0.830(15)	1.92(3)	2.700(5)	155(6)
O5–H51···O12	0.82	2.01	2.821(5)	167.7
O5–H52···O11^{g}	0.82	2.00	2.776(4)	156.3
O6–H61···O24^{e}	0.82	2.17	2.961(5)	161.8
O7–H71···O14^{c}	0.813(16)	1.98(4)	2.700(5)	148(6)
O7–H72···O23^{e}	0.82	2.17	2.882(4)	145.8
O8–H82···O21^{b}	0.825(16)	1.98(2)	2.784(4)	165(6)
O8–H81···O12^{c}	0.82	1.90	2.706(4)	166.4

Note: Symmetry code: $^{a}x+1, y, z$; $^{b}x-1, y, z$; $^{c}x, y-1, z$; $^{d}x+1, y-1, z$; $^{e}x-1, y+1, z$; $^{f}-x+1, -y+1, z$; $^{g}-x+2, -y+1, -z$; $^{h}-x+2, -y, -z$.

Coordinated water molecules are donors in an extended network of H bonds with lengths ranging from 2.68 to 3.00 Å. The acceptors are carboxylate and coordinated water O atoms. The relevant geometrical parameters are listed in table 3.

The polymeric structure of CAQUIN 2 is also composed of molecular ribbons. They propagate in the *c* direction of the unit cell, as illustrated in figure 3. The ribbons are built up of structural units as shown in figure 4 with atom labeling. Each Ca(II) is chelated by a N,O-bonding moiety of the ligand molecule denoted as (2) – atoms N21 and O21, the second oxygen atom of this carboxylate group O22 does not participate in coordination, similar to the other carboxylate group of this ligand (C28/C23/C24) which remains protonated. Bridging of Ca(II) occurs through the ligand molecule denoted as (1), which uses its bidentate carboxylate group (C17/O11/O12): O11 – Ca and O12 – Ca$^{(i)}$ (for symmetry code, see table 4). In addition, the carboxylate O13

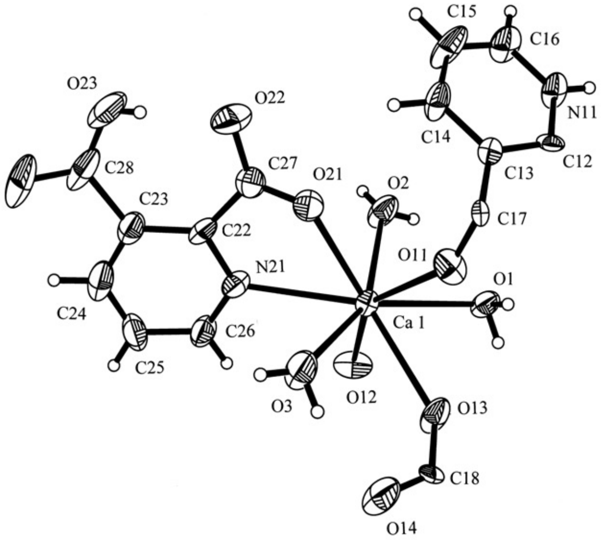

Figure 3. The alignment of molecular ribbons in the structure of *catena*-trisaquo[(μ-2,3-dicarboxypyridin-1-ium-*O*,*O*′; *O*″)(*H* pyridine-2,3-dicarboxylato-*N*,*O*)]calcium(II).

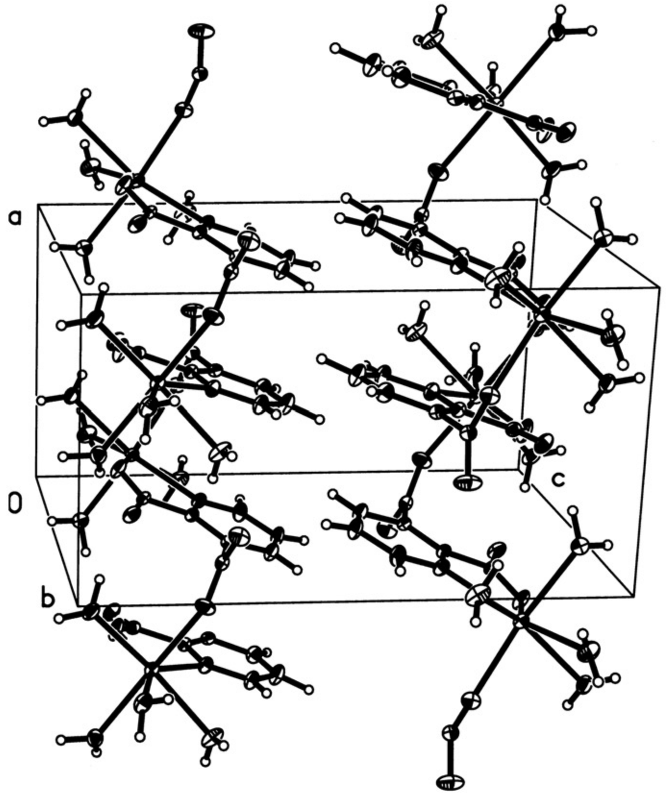

Figure 4. A structural unit of catena-trisaquo[(μ-2,3-dicarboxypyridin-1-ium-*O*,*O*′; *O*″)(H pyridine-2, 3-dicarboxylato-*N*,*O*)]calcium(II) with atom labels.

Table 4. Selected bond distances and angles (Å, °) around Ca(II) ions in the structure of CAQUIN 2 complex.

Ca–N21	2.706(7)	O21–Ca–N21	60.9(2)
Ca–O21	2.408(6)	N21–Ca–O3	71.3(2)
Ca–O11	2.346(8)	O3–Ca–O12	101.9(3)
Ca–O12	2.321(8)	O12–Ca–O13	76.8(3)
Ca–O13	2.553(5)	O13–Ca–O1	67.7(2)
Ca–O1	2.681(5)	O1–Ca–O11	73.5(3)
Ca–O2	2.353(5)	O11–Ca–O2	95.0(3)
Ca–O3	2.371(6)	O2–Ca–O21	72.9(3)

donated by the (C18/C13/C14) group is also coordinated to the Ca while the O14 does not take part in coordination. As a whole, ligand molecule (1) is univalent, since a proton has been detected to be attached to the hetero-nitrogen atom N11. Three water oxygens (O1, O2, O3) complete the coordination around the Ca(II) ion to eight. The resulting coordination polyhedron is a capped pentagonal bipyramid with a strongly distorted equatorial plane (r.m.s. 0.3992 Å) composed of the following atoms (with shifts from the mean plane): O13(−0.6865 Å), O11(+0.2713 Å), O12(+0.6433 Å), N21(-0.5110 Å), and O21(+0.0495 Å), the O3 atom forming a single apex on one side and O1 and O2 atoms – two apices on the other. The relevant bond distances and angles are collected in table 4. The observed bond distances and angles within both ligands are close to those reported for the parent acid [13]. The pyridine-ring of ligand (1) is planar (r.m.s. 0.0113 Å); the carboxylate groups (C17/O11/O12) and (C18/O13/14) have dihedral angles of 86.6(2)° and 4.7(2)° with it, respectively. The pyridine ring of ligand molecule (2) is also planar (r.m.s. 0.0123 Å), its carboxylate groups form dihedral angles of 21.8(2)° (C27/O21/O22) and 17.0(2)° (C28/O23/O24). The pyridine rings of ligands (1) and (2) are inclined to each other by 63.1(2)°.

The protonated carboxylate O23 forms a strong intramolecular H bond of 2.423(12) Å to the carboxylate O22 belonging to the same ligand molecule. Weaker H bonds with distances in the range 2.713(8) to 2.906(8) Å are also observed between coordinated water O atoms and carboxylate O atoms of the same structural unit. Coordinated water molecules participate as donors in a H bond network in which the acceptors are carboxylate O atoms of adjacent ligands. The hetero-ring N11 and the attached H111 are active in two bonds: one to a coordinated water O1$^{(iv)}$, the other – to the carboxylate O14$^{(ii)}$ atom, each belonging to a different adjacent ligand. For details, see table 5.

The structures of CAQUIN 1 and CAQUIN 2 indicate that they are different phases, not polymorphs. In both, the ligand molecules are bridging, however, in different ways. In both, chelation to Ca(II) leads to significant deformation of the ligand geometry compared to the parent acid. This effect concerns, first of all, the carboxylate groups taking part in bridging. While in the structure of quinolinic acid the carboxylic groups are twisted out of the pyridine-ring plane by −8.3(2)° and +10.8(2)° [13], the relevant angles in CAQUIN 1 are −9.4(1)° and −91.1(1)° (ligand 1) and −6.4(1)° and −82.9(1)° (ligand 2) and to −9.4(2)° and +91.1(2)° (ligand 1) and to 21.8(2)° and 17.0(2)° (the non-bridging ligand 2) in the structure of CAQUIN 2.

Two other azine dicarboxylate ligands show the same size and geometry as the title ligand: pyridine-3,4-dicarboxylate and pyrazine-2,3-dicarboxylate. The structure of

Table 5. Geometrical parameters (Å, °) of hydrogen bonds in the structure of CAQUIN 2.

	D–H	H···A	D–H···A	D–H–A
O23–H231···O22	0.82	1.74	2.423(11)	139.6
O1–H11···O12[b]	0.82	2.45	2.993(10)	124.8
O1–H12···O11[f]	0.82	2.12	2.932(9)	174.2
O2–H21···O1	0.82	2.39	2.826(7)	114.6
O2–H21···O14[a]	0.82	2.13	2.794(7)	138.7
O2–H22···O24[e]	0.824(17)	2.03(6)	2.740(8)	144(11)
O3–H31···O14	0.82	1.92	2.716(8)	163.8
O3–H31···O13	0.82	2.52	2.911(8)	110.7
O3–H32···O23[c]	0.827(17)	2.12(4)	2.916(9)	163(13)
N11–H111···O1[e]	0.86	2.07	2.864(7)	153.7
N11–H111···O14[d]	0.86	2.25	2.622(7)	105.8

Note: Symmetry code: [a]$x, y+1, z$; [b]$x-1/2, -y, -z+1$; [c]$x, y-1/2, -z+1/2$; [d]$x-1/2, -y+1, -z+1$; [e]$x, y+1/2, -z+1/2$; [f]$x+1/2, -y, -z+1$.

a Ca(II) complex with the first ligand is also built up of molecular ribbons in which the bridging of Ca(II) proceeds *via* both O atoms of the carboxylate group in position "3," each bidentate coordinating two metal ions. The other carboxylate group does not participate in coordinating [3]. The carboxylate groups form dihedral angles of 57.6(1)° (the bridging COO group) and 54.6(1)° (the uncoordinated COO group) with the pyridine ring. Since the relevant values reported for parent acid are 39.8° and 73.0° [14], the influence of the coordination mode on the geometry of the ligand is clearly visible.

A different bridging mode has been reported in the Ca(II) complex with pyrazine-2, 3-dicarboxylate [15] in which the bridging proceeds through a single ligand molecule. Its N,O-bonding moiety coordinates a Ca(II) ion and both O atoms of the second carboxylate group chelate another Ca(II) ion. Molecular ribbons can thus be imagined. However, the second carboxylate O atom of the group contributing one O atom to the N,O-bonding moiety is bonded to a Ca(II) ion in an adjacent ribbon "above," while one of the carboxylate O atoms of the second group is bidentate and bonded to a Ca(II) ion in a ribbon "below". Molecular layers are formed in this way. The carboxylate group participating in the N,O-bonding moiety forms a dihedral angle of 51.9(1)° with the pyrazine-ring plane, the second group – an angle of 96.0(1)° as compared to the respective dihedral angles in the molecule of pyrazine-2,3-dicarboxylic acid dihydrate, 33.7° [16]. These results indicate that coordination to Ca(II) does not affect the pyridine or pyrazine ring geometry but introduces significant changes in the values of dihedral angles formed with the rings by planes of carboxylate groups, particularly those taking part in bridging.

The structures of both compounds conform with the tendency observed in the structures of Ca(II) complexes with other pyridine dicarboxylate ligands to adopt different coordination geometries of the Ca(II) ion and to form catenated molecular patterns with diverse bridging modes depending on the relative positions of chelating sites in the ligand molecules.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 697000 (CAQUIN 1) and CCDC 697001 (CAQUIN 2). Copies of the available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-(0)1223-336033 or Email: teched@chemcrys.cam.ac.uk).

References

[1] J.K. Jaisval. *J. Biosci*., **26**, 357 (2001).
[2] H. Einspahr, C.E. Bugg. *Acta Cryst*., **B37**, 1044 (1981).
[3] W. Starosta, H. Ptasiewicz-Bąk, J. Leciejewicz. *J. Coord. Chem*., **52**, 265 (2001).
[4] W. Starosta, H. Ptasiewicz-Bąk, J. Leciejewicz. *J. Coord. Chem*., **55**, 985 (2002).
[5] W. Starosta, H. Ptasiewicz-Bąk, J. Leciejewicz. *J. Coord. Chem*., **56**, 33 (2003).
[6] G. Srtrahs, R.E. Dickerson. *Acta Cryst*., **B24**, 571 (1968).
[7] W. Starosta, H. Ptasiewicz-Bąk, J. Leciejewicz. *J. Coord. Chem*., **55**, 873 (2002).
[8] W. Starosta, H. Ptasiewicz-Bąk, J. Leciejewicz. *J. Coord. Chem*., **55**, 1147 (2002).
[9] W. Starosta, H. Ptasiewicz-Bąk, J. Leciejewicz. *J. Coord. Chem*., **55**, 1 (2002).
[10] W. Starosta, H. Ptasiewicz-Bąk, J. Leciejewicz. *J. Coord. Chem*., **55**, 469 (2002).
[11] Oxford Diffraction. *CrysAlis RED*, Oxford Diffraction Ltd., United Kingdom (2008).
[12] G.M. Sheldrick. *Acta Cryst*., **A64**, 112 (2008).
[13] T. Takusagawa, K. Hirotsu, A. Shimada. *Bull. Chem. Soc. Jpn*, **46**, 2372 (1973).
[14] T. Takusagawa, K. Hirotsu, A. Shimada. *Bull. Chem. Soc. Jpn*, **46**, 2669 (1973).
[15] W. Starosta, J. Leciejewicz. *J. Coord. Chem*., **58**, 963 (2005).
[16] T. Takusagawa, A. Shimada. *Chem. Lett*., 1121 (1973).