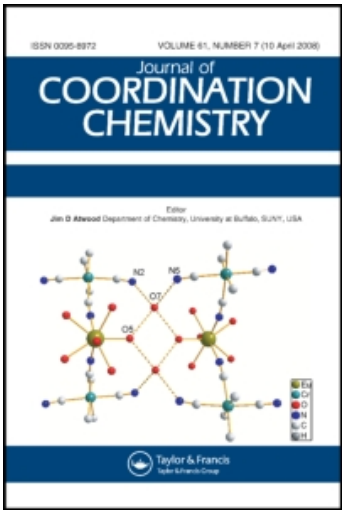

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MOLECULAR RIBBONS COMPOSED OF CALCIUM(II) IONS BRIDGED BY CARBOXYLATE AND WATER OXYGEN ATOMS IN THE CRYSTALS OF Ca(II) COMPLEX WITH 5-METHYLPYRAZINE-2-CARBOXYLATE LIGANDS

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MOLECULAR RIBBONS COMPOSED OF CALCIUM(II) IONS BRIDGED BY CARBOXYLATE AND WATER OXYGEN ATOMS IN THE CRYSTALS OF Ca(II) COMPLEX WITH 5-METHYLPYRAZINE-2-CARBOXYLATE LIGANDS

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Crystals of monoaquo(μ-5-methylpyrazine-2-carboxylato-N,O,O′)(5-methylpyrazine-2-carboxylato-N,O)di(μ-aquo-O,O)calcium(II) contain molecular ribbons in which two adjacent calcium(II) ions are bridged by two bidentate oxygen atoms donated by two ligand molecules on one side and bidentate oxygen atoms of two water molecules on the other. The coordination polyhedron around the Ca(II) ion is a pentagonal bipyramid. The vertices of its pentagonal base are composed of two bridging water oxygen atoms, two carboxylate oxygen atoms of two ligand molecules and a nitrogen atom belonging to one of the bridging ligands. A coordinated water molecule constitutes the apex of the pyramid on one side of the base, while the N,O bonding moiety of a second ligand molecule makes two apices on the other side of the base. The ribbons are held together by a system of hydrogen bonds.

Keywords: 5-Methylpyrazine-2-carboxylic acid; calcium complex; X-ray structure analysis

INTRODUCTION

Monomeric molecules were found in crystals of the calcium complex with pyrazine-2-carboxylic acid (PZCA).[1] However, the structure of the calcium complex with 3-aminopyrazine-2-carboxylic acid (APZA) revealed a polymeric molecular pattern in which one carboxylic oxygen atom, apart

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from chelating the central ion, also acts as a bridge.[2] This observation may be considered as due to the spatial disturbance of the neighborhood of the carboxylic group introduced by the non-bonding amino group. To recognize whether the size of the pyrazine ligand influences the molecular patterns observed in its calcium complexes, an X-ray structural study has been undertaken of the calcium complex with 5-methylpyrazine-2-carboxylic acid (MPZA). In this ligand the non-bonding methyl group is situated at a distinctly larger distance from the chelating N,O bonding moiety than in the case of the aminopyrazinic ligand.

EXPERIMENTAL

The title compound was obtained by dissolving 1 millimole of calcium carbonate (analytical grade) in 50 mL of a boiling aqueous solution containing 2 millimoles of MPZA (Aldrich). The solution was boiled for 1 h and then left to evaporate to dryness at room temperature. Colorless single crystals in the form of rectangular plates separated after a few days. The dimensions of a crystal taken for collecting X-ray diffraction data are given in Table I.

X-ray reflections were measured at room temperature using KUMA KM4 (MoK_α radiation) four circle diffractometer operating in $\omega - 2\theta$ mode. Two standard reflections were monitored every 200 reflections. They remained constant throughout the data collection process. 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; those with $(I/\sigma^2(I) > 4.0)$ were used in the refinement. An empirical absorption correction based on an ellipsoidal fit to selected strong reflections was applied. Non-hydrogen ions were located by direct methods using the SHELXLS program[3] and the hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2 by the 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 weighing scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (A * P)^2 + B * P]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. A, B are refined parameters listed in Table I. Calculations were carried out using SHELXL97.[4] Final atomic coordinates and equivalent isotropic displacements are listed in Table II and 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.

TABLE I Crystal data and structure refinement details for $Ca(MPZA)_2(H_2O)_2$

Empirical formula	$C_{12}H_{14}N_4O_6Ca$
Formula weight	350.29
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.773(2)$ Å
	$b = 8.792(2)$ Å
	$c = 12.142(2)$ Å
	$\alpha = 83.77(3)°$
	$\beta = 77.94(3)°$
	$\gamma = 70.17(3)°$
	$V = 762.72$ Å^3
Z	2
Calculated density	1.525 g cm^{-3}
μ (MoKα)	0.45 mm^{-1}
F(000)	364.0
Crystal size	(0.1 × 0.5 × 0.5) mm^3
Max 2θ for data collection	70.17°
Index range	$0 \leq h \leq 12, -13 \leq k \leq 14, -19 \leq l \leq 19$
No. of measured reflections	5379
No. of reflections with $F_o > 4\sigma(F_o)$	4734
R_{int}	0.027
Method of structure solution	Direct method
Method of structure refinement	Full-matrix least squares on F^2
No. of parameters refined	265
Goodness-of-fit on F^2	0.901
Final R1 [$F_o > 4\sigma(F_o)$]	0.035
Final wR2 index	0.107
Absorption correction	Experimental
Min. and max. transmission factors	0.639, 0.867
Largest diff. peak and hole	0.69 e/Å^3 and −0.32 e/Å^3
Weight parameters (A, B)	0.1000, 0.00
Mean shift/esd	0.022

DISCUSSION

A remarkable feature of the molecular pattern observed in the crystals of the title compound is the presense of three-dimensional molecular ribbons. Figure 1 illustrates how the ribbons are packed in the crystal; a fragment of the ribbon with numbering of atoms is shown in Figure 2. Ca(II) ions are bridged alternatively by two bidentate oxygen atoms from water molecules and by two bidentate oxygen atoms, each donated by the carboxylic groups of MPZA ligands. The coordination around the Ca(II) ion is eightfold. The metal ion, the two bridging water oxygen atoms [Ca–O1 2.627(1) Å, Ca–O1^{II} 2.496(1) Å], the two bridging carboxylate oxygen atoms [Ca–O11 2.457(1) Å and Ca–O11^{I} 2.547(1) Å] and the heteroring nitrogen atom belonging to the bridging ligand MPZA1 [Ca–N11 2.587(1) Å] make a

TABLE II Fractional atomic coordinates and equivalent isotropic displacement ($Å^2$) for $Ca(MPZA)_2(H_2O)_2$

Atom	*x*	*y*	*z*	U_{eq}
Ca	0.7708 (3)	0.4784 (2)	0.4432 (2)	0.0198 (6)
O1	1.0248 (1)	0.6218 (1)	0.41295 (7)	0.0242 (2)
O2	0.6231 (1)	0.7539 (1)	0.4864 (1)	0.0404 (3)
O11	0.4727 (1)	0.5324 (1)	0.38224 (7)	0.0253 (1)
O12	0.3085 (1)	0.5934 (1)	0.24239 (8)	0.0284 (2)
O21	0.7406 (1)	0.2167 (1)	0.4457 (1)	0.0365 (2)
O22	0.8316 (2)	−0.0450 (1)	0.4091 (1)	0.0417 (3)
N11	0.7701 (1)	0.5846 (1)	0.23600 (9)	0.0285 (2)
N12	0.7273 (2)	0.7062 (2)	0.0167 (1)	0.0451 (3)
N21	1.0654 (1)	0.2468 (1)	0.3348 (9)	0.0279 (2)
N22	1.3451 (2)	−0.0222 (2)	0.2360 (2)	0.0593 (5)
C11	0.6129 (1)	0.6054 (1)	0.19920 (9)	0.0237 (2)
C12	0.5950 (2)	0.6623 (2)	0.0890 (1)	0.0391 (3)
C13	0.8815 (2)	0.6927 (2)	0.0550 (1)	0.0343 (3)
C14	0.9036 (2)	0.6271 (2)	0.1632 (1)	0.0356 (3)
C15	0.4523 (1)	0.5737 (1)	0.28138 (9)	0.0212 (2)
C17	1.0284 (3)	0.7481 (3)	−0.0219 (2)	0.0512 (4)
C21	1.0389 (2)	0.1028 (1)	0.3388 (1)	0.0266 (2)
C22	1.1762 (3)	−0.0277 (2)	0.2869 (2)	0.0544 (5)
C23	1.3739 (2)	0.1184 (2)	0.2345 (l)	0.0362 (3)
C24	1.2319 (2)	0.2522 (2)	0.2815 (1)	0.0347 (3)
C25	0.8558 (2)	0.0899 (1)	0.4028 (1)	0.0273 (2)
C27	1.5618 (3)	0.1282 (3)	0.1799 (2)	0.0554 (5)
H1	1.109 (4)	0.621 (3)	0.349 (2)	0.055 (6)
H2	0.983 (3)	0.711 (2)	0.416 (2)	0.033 (5)
H3	0.513 (4)	0.762 (3)	0.505 (3)	0.080 (9)
H4	0.659 (4)	0.832 (3)	0.463 (2)	0.056 (7)
H12	0.486 (4)	0.676 (4)	0.062 (2)	0.068 (8)
H14	1.019 (3)	0.611 (3)	0.187 (2)	0.047 (6)
H15	1.050 (4)	0.713 (4)	−0.094 (3)	0.083 (9)
H16	1.101 (9)	0.739 (8)	0.010 (5)	0.20 (3)
H17	0.977 (5)	0.859 (4)	−0.017 (3)	0.082 (9)
H22	1.163 (4)	−0.133 (3)	0.291 (2)	0.057 (7)
H24	1.244 (3)	0.349 (3)	0.278 (2)	0.045 (6)
H25	1.585 (6)	0.225 (5)	0.210 (4)	0.13 (1)
H26	1.587 (4)	0.086 (3)	0.103 (3)	0.070 (8)
H27	1.633 (5)	0.052 (4)	0.205 (3)	0.077 (9)

deformed pentagon. The pentagons around adjacent Ca ions are linked by common edges – the bridging oxygen atoms. In addition, each Ca(II) ion is chelated by a second ligand molecule (MPZA2) via its N,O bonding moiety [Ca–O21 2.387(1) Å, Ca–N21 2.699(2) Å]. Both MPZA ligands are almost planar with r.m.s of 0.071 Å for the MPZA1 molecule and 0.042 Å for MPZA2, however, in the MPZA1 ligand the bridging carboxylate oxygen atom O11 and the methyl carbon atom C17 deviate from the mean plane by 0.130 and 0.131 Å, respectively. The planes of MPZA1 and MPZA2 ligands make the angle of 86.4(1)°. The coordination is completed by an oxygen

TABLE III Selected bond lengths (Å) and angles (°) for $Ca(MPZA)_2(H_2O)_2$

Calcium(II) coordination					
Ca–O11	2.457 (1)	O11–Ca–O1	135.75 (3)		
Ca–N11	2.451 (1)	O11–Ca–N11	65.88 (4)		
Ca–O11^{I}	2.547 (1)	O11–Ca–O1^{I}	151.23 (3)		
Ca–O1	2.627 (1)	O11–Ca–O2	79.20 (5)		
Ca–O1^{II}	2.497 (1)	O2–Ca–O1	71.19 (4)		
Ca–O21	2.387 (1)	O2–Ca–O21	147.08 (4)		
Ca–N21	2.699 (2)	O21–Ca–N21	116.37 (4)		
Ca–O2	2.366 (1)	O1–Ca–O1^{II}	69.03 (4)		
Ligand molecules					
C11–C12	1.395 (2)	N11–C11–C12	120.6 (1)		
C12–N12	1.340 (2)	C11–C12–N12	122.8 (1)		
N12–C13	1.338 (2)	C12–N12–C13	116.7 (1)		
C13–C14	1.397 (2)	N12–C13–C14	120.3 (1)		
C14–N11	1.344 (2)	C13–C14–N11	122.9 (1)		
N11–C11	1.336 (2)	C14–N11–C11	116.5 (1)		
C13–C17	1.499 (2)				
C17–H15	0.93 (3)				
C17–H16	0.72 (6)				
C17–H17	0.92 (4)				
C11–C15	1.512 (2)	O11–C15–012	126.0 (1)		
C15–O11	1.266 (1)				
C15–012	1.255 (1)				
C21–C22	1.378 (2)	N21–C21–C22	120.6 (1)		
C22–N22	1.343 (2)	C21–C22–N22	122.8 (1)		
N22–C23	1.326 (2)	C22–N22–C23	116.8 (1)		
C23–C24	1.389 (2)	N22–C23–C24	120.2 (1)		
C24–N21	1.334 (2)	C23–C24–N21	123.3 (1)		
N21–C21	1.344 (1)	C24–N21–C21	116.1 (1)		
C22–C27	1.499 (2)				
C27–H25	1.04 (4)				
C27–H26	1.00 (3)				
C27–H27	0.79 (3)				
C21–C25	1.507 (2)	O21–C25–O22	125.7 (1)		
C25–O21	1.253 (2)				
C25–O22	1.254 (2)				
Water molecules					
O1–H1	0.90 (3)	H1–O1–H2	97 (2)		
O1–H2	0.74 (2)				
O2–H3	0.82 (3)	H3–O2–H4	123 (3)		
O2–H4	0.83 (3)				
Hydrogen bonds					
O1–H1···O12^{IV}	2.65 (1)	H1···O12^{IV}	2.06 (1)	O1–H1–O12^{IV}	167.1 (1)
O1–H2···O22^{III}	2.80 (1)	H2···O22^{III}	2.07 (1)	O1–H2–O22^{III}	169.8 (1)
O2–H3···O21^{I}	2.71 (1)	H3···O21^{I}	1.88 (1)	O2–H3–O21^{I}	177.7 (1)
O2–H4···O22^{III}	2.75 (1)	H4···O22^{III}	1.96 (1)	O2–H4–O22^{III}	158.6 (1)

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

atom of a water molecule [Ca–O2 2.367(1) Å] situated on the other side of the pentagon with the Ca–O2 bond almost perpendicular to it (see Table III).

The bond distances and angles in both MPZA ligands compare favorably with those reported for the parent acid.[5]

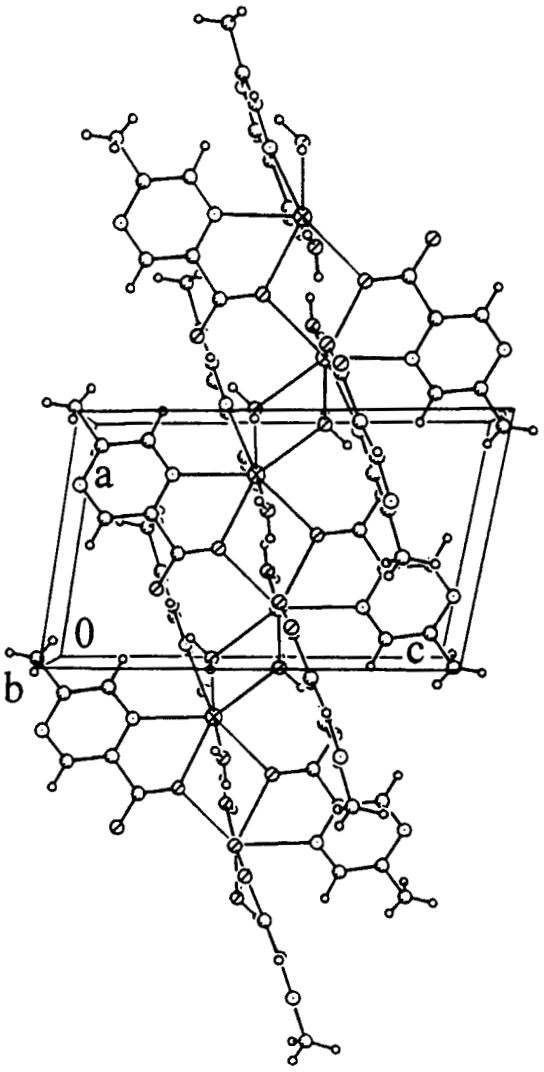

FIGURE 1 The packing of molecular ribbons in the structure of $Ca(MPZA)_2(H_2O)_2$.

The molecular ribbons observed in the title compound are held together by hydrogen bonds which link both the bridging and coordinated water molecules with non-bonded oxygen atoms belonging to the carboxylate groups of adjacent MPZA ligands. The respective bond lengths and angles are listed in Table III. The hydrogen atoms attached to the carbon atoms do not take part in the hydrogen-bond system.

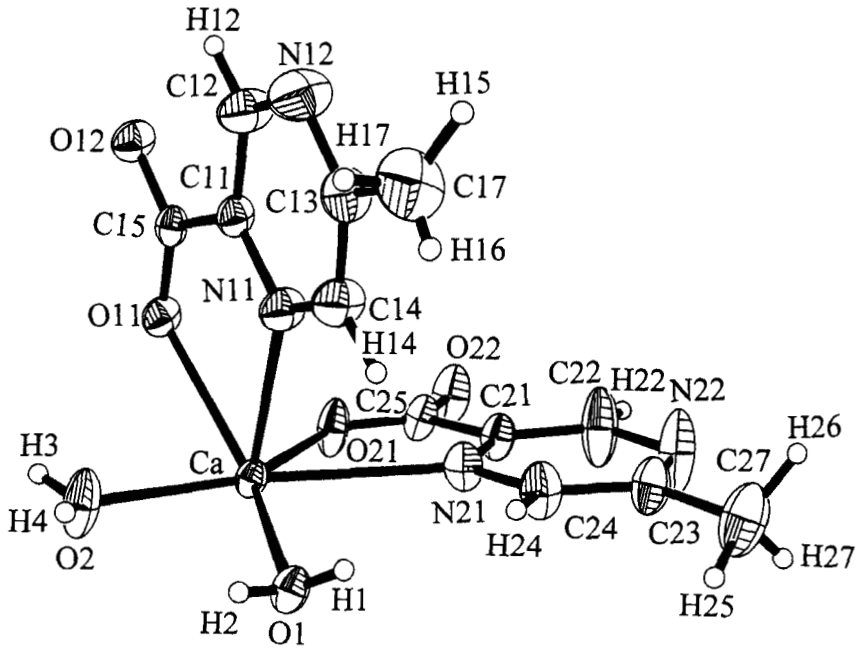

FIGURE 2 The structural unit of $Ca(MPZA)_2(H_2O)_2$ with numbering of atoms. The non-H atoms are shown as 50% probability ellipsoids.

Bridging by bidentate carboxylate oxygen atoms has also been found in the structure of a calcium compound with pyrazine-2,3-dicarboxylic (2,3-PZDC) ligand,[6] but the bridging system is different. Both oxygen atoms of one of the carboxylic groups belonging to the 2,3-PZDC ligand are bound. Thus, two adjacent Ca(II) ions are doubly bridged with different mean Ca–O bond distances (2.346 and 2.604 Å). Simultaneously, this carboxylic group is also bridging giving rise to molecular ribbons. The second carboxylic group of each 2,3-PZDC ligand is coordinated to the Ca(II) ion only via its N,O bonding moiety. Two water molecules coordinated to each Ca(II) ion do not take part in the bridging system.

Both oxygen atoms of the carboxylic group in the structure of the Ca(II) complex with aminopyrazinic ligand[1] take part in bridging. In this compound, however, the carboxylate group is bidentate and a two-dimensional pattern is observed in the crystals of this compound.[2]

The presence of a polymeric crystal structure in the title compound may be an indication that the steric disturbance brought about by the size of the ligand plays a significant role in setting up the molecular patterns in calcium complexes with pyrazinate ligands.

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