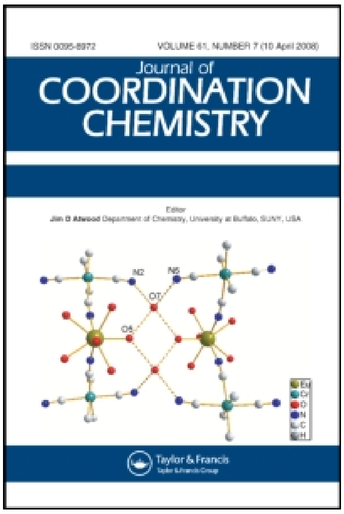
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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 Ca(II) (pyrazine-2,3-dicarboxylate) tetrahydrate chloride

Wojciech Starosta[a]; Janusz Leciejewicz[a]

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

To cite this Article Starosta, Wojciech and Leciejewicz, Janusz(2004) 'The crystal structure of Ca(II) (pyrazine-2,3-dicarboxylate) tetrahydrate chloride', Journal of Coordination Chemistry, 57: 13, 1151 — 1156

To link to this Article: DOI: 10.1080/00958970420002619177

URL: http://dx.doi.org/10.1080/00958970420002619177

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., Vol. 57, No. 13, 10 September 2004, pp. 1151–1156

Taylor & Francis
Taylor & Francis Group

THE CRYSTAL STRUCTURE OF CA(II) (PYRAZINE-2,3-DICARBOXYLATE) TETRAHYDRATE CHLORIDE

WOJCIECH STAROSTA and JANUSZ LECIEJEWICZ*

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

(Received 27 February 2004; In final form 28 June 2004)

Crystals of *catena*-[(tetraqua-*O*)(μ-hydrogen pyrazine-2,3-dicarboxylate-N,O,N′,O′)calcium(II)] chloride contain molecular ribbons composed of polycations $\{Ca[H(2,3\text{-}PZDC](H_2O)_4\}_n^+$ and chloride Cl^- anions. Two adjacent Ca(II) atoms are bridged by a ligand molecule which uses both its N,O bonding moieties. One of the carboxylic groups retains its hydrogen atom which takes part in a short [D–H $\cdots$ A 2.378(2) Å] intramolecular hydrogen bond. The coordination polyhedron around Ca(II) is a distorted pentagonal bipyramid with two apices on one side of the pentagonal equatorial plane and one apex on the other. Chloride anions are located in the interstitial space between the ribbons.

Keywords: Pyrazine-2,3-dicarboxylic acid; Calcium complex; X-ray diffraction; Crystal structure

INTRODUCTION

Crystal-structure studies of complexes with pyridine-2,6-dicarboxylate and pyridine-3,5-dicarboxylate ligands have revealed a tendency to form compounds with a number of polymeric molecular patterns [1,2]. The structures of three Ca(II) complexes with pyrazine-2,6-dicarboxylate have been reported [3,4]. Only one Ca(II) complex with pyrazine-2,3-dicarboxylate (2,3-PZDC) has been previously obtained and its crystal structure determined. Since our previous experience with Ca(II) compounds containing azine dicarboxylate ligands has shown that the appearance of a particular phase depends on the calcium compound used for chemical synthesis, we have performed a series of experiments aimed at preparing new Ca(II) compounds with pyrazine-2,3-dicarboxylate ligands. We have obtained and grown single crystals of a new compound whose crystal structure is reported in this paper.

---

*Corresponding author. E-mail: jlec@orange.ichtj.waw.pl

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897042000261917

EXPERIMENTAL

Hot aqueous solutions, one containing 1 mmol of pyrazine-2,3-dicarboxylic acid dihydrate (Aldrich) and the other 1 mmol anhydrous calcium dichloride were mixed and boiled with stirring for 1 h. After evaporation at room temperature, the deposited crystalline material was dissolved in warm methanol. Colorless, rectangular single crystals were formed overnight. The dimensions of a single crystal selected 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 in the 2θ range from 15 to 30°. Reflections were processed using profile analysis and corrected for Lorentz and polarization effects. An absorption correction based on a ψ-scan was applied. Nonhydrogen atoms were located by direct methods using the SHELXLS program [6] and hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2 by full-matrix least-squares (program SHELXL97 [7]) was done on positional parameters of all atoms, anisotropic vibrational parameters of all non-H atoms and isotropic temperature factors of hydrogen atoms. A weighting scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (A \times P)^2 + B \times P]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. A, B are the parameters listed in Table I. Selected bond lengths and angles are collected in Table II.

TABLE I Crystal data and structure refinement details for $\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+Cl^-$

Empirical formula	$C_6H_{11}N_2O_8CaCl$
Formula weight	314.69
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$Pbca$
Unit cell dimensions (Å)	$a = 11.714(2)$ $b = 14.213(3)$ $c = 14.589(3)$
V (Å^3)	2428.9
Z	8
Calculated density (g cm^{-3})	1.721
μ (Mo Kα) (mm^{-1})	0.77
$F(000)$	1296.0
Crystal size (mm^3)	$0.20 \times 0.14 \times 0.43$
Max 2θ for data collection (°)	60.18
Index range	$-16 \leq h \leq 0$, $-20 \leq k \leq 0$, $-20 \leq l \leq 0$
No. of measured reflections	3567
No. of unique reflections with $F_o > 4\sigma(F_o)$	2608
R_{int}	0.020
Method of structure solution	direct method
Method of structure refinement	full-matrix least squares on F^2
No. of parameters refined	207
Goodness-of-fit on F^2	1.058
Final $R1$ $[F_o > 4\sigma(F_o)]$	0.0346
Final $wR2$ index	0.1106
Absorption correction	ψ-scan
Min. and max. transmission	0.784, 0.847
Largest diff. peak and hole (e Å^{-3})	0.51, −0.27
Weight parameters (A,B)	0.0732, 0.33
Mean shift/esd	0. 000

TABLE II Selected bond lengths (Å) and angles (°) for $\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+Cl^-$

Ca(II) coordination			
Ca–O(1)	2.398(1)	N(1)–Ca–N(1)	59.51(4)
Ca–N(1)	2.792(1)	N(1)–Ca–O(3)	72.51(4)
Ca–O(3)	2.350(1)	O(3)–Ca–N(2)	59.92(4)
Ca–N(2)	2.777(1)	N(2)–Ca–O(7)	80.73(5)
Ca–O(5)	2.393(1)	O(7)–Ca–O(5)	70.85(6)
Ca–O(6)	2.354(1)	O(5)–Ca–N(1)	73.87(5)
Ca–O(7)	2.417(1)	O(7)–Ca–O(6)	84.25(5)
Ca–O(8)	2.484(1)	O(8)–Ca–O(1)	69.01(4)
Ligand molecule			
N(1)–C(2)	1.344(2)	C(6)–N(1)–C(2)	117.8(1)
C(2)–C(3)	1.396(2)	N(1)–C(2)–C(3)	120.6(1)
C(3)–N(2)^{I}	1.344(2)	C(2)–C(3)–N(2)^{I}	120.7(1)
N(2)–C(5)	1.320(2)	C(3)–N(2)^{I}–C(5)	117.8(1)
C(5)–C(6)	1.388(2)	N(2)^{I}–C(5)–C(6)	121.4(1)
C(6)–N(1)	1.321(2)	C(5)–C(6)–N(1)	121.5(1)
C(2)–C(7)	1.517(2)		
C(7)–O(1)	1.221(2)	O(1)–C(7)–O(2)	121.1(2)
C(7)–O(2)	1.274(2)		
O(2)–H(21)	1.154(2)		
C(3)–C(8)	1.520(2)		
C(8)–O(3)	1.229(2)	O(3)–C(8)–O(4)	121.9(2)
C(8)–O(4)	1.267(2)		
Coordinated water molecules			
O(5)–H(51)	0.85(3)	H(51)–O(5)–H(52)	106(3)
O(5)–H(52)	0.75(4)		
O(6)–H(61)	0.79(3)	H(61)–O(6)–H(62)	110(3)
O(6)–H(62)	0.90(3)		
O(7)–H(71)	0.83(3)	H(71)–O(7)–H(72)	99(3)
O(7)–H(72)	0.82(3)		
O(8)–H(81)	0.83(4)	H(81)–O(8)–H(82)	109(3)
O(8)–H(82)	0.84(3)		
Hydrogen bonds			
D–H···A	d(D–H···A)	∠(D–H–A)	
O(2)–H(21)···O(4)^{II}	2.378(2)	172(3)	
O(6)–H(61)···O(3)^{III}	2.854(2)	175(3)	
O(7)–H(71)···O(1)^{III}	2.975(2)	155(3)	
O(8)–H(82)···O(4)^{IV}	2.967(2)	165(3)	

Equivalent positions:
^{I} $x, -y+3/2, z-1/2$; ^{II} $x, -y+3/2, z+1/2$; ^{III} $x+1/2, y, -z+3/2$; ^{IV} $-x, y-1/2, -z+3/2$.

DISCUSSION

The structural building blocks observed in the title compound are polycationic ribbons composed of Ca(II) atoms bridged by pyrazine-2,3-dicarboxylate (2,3-PZDC) molecules. Chlorides are located in the interstitial space between the ribbons. The alignment of the ribbons in the unit cell is illustrated in Fig. 1, which for clarity shows only two ribbons. The environment of a Ca(II) atom is shown in Fig. 2 which also contains the atom labeling scheme. The ligand molecule donates both its N,O bonding moieties to bridge adjacent Ca(II) atoms, resulting in an infinite molecular chain propagating in the *a* axis. In addition, each Ca(II) atom coordinates with four water oxygen atoms raising the coordination number to eight. The relevant Ca–N and Ca–O bond distances and angles listed in Table II are close to those reported for other complexes with diazine carboxylate ligands. The coordination polyhedron is a distorted pentagonal bipyramid

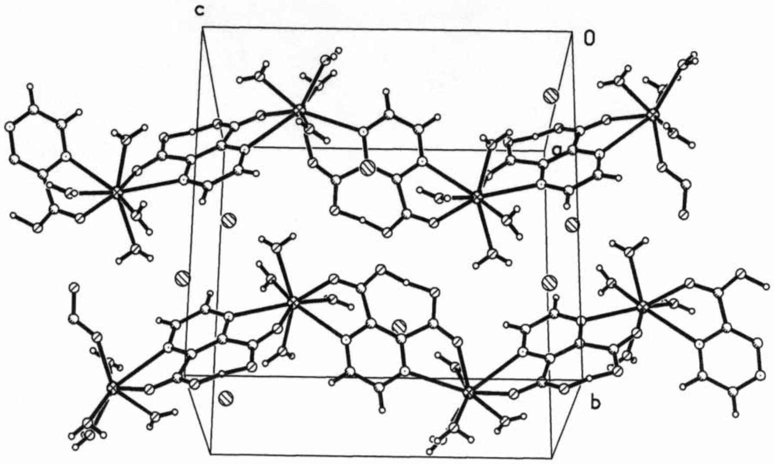


FIGURE 1 The alignment of molecular ribbons in the crystal of $\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+Cl^-$. For clarity, only two ribbons are shown.

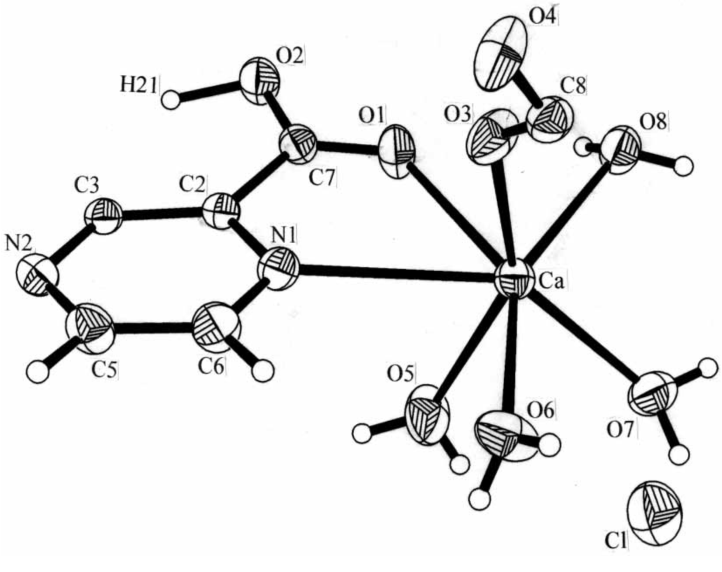


FIGURE 2 The structural unit $\{Ca[H(2,3\text{-}PZDC)](H_2O)_4\}^+Cl^-$ with atom labeling scheme. The non-hydrogen atoms are shown as 50% probability ellipsoids.

with one apex on one side of the equatorial plane and two on the other. The equatorial plane is formed by Ca, O(3), O(5), O(7), N(1) and N(2^I) atoms and exhibits a rather large deviation from planarity, since the maximum and minimum shifts from the average plane are +0.390(1) Å [N(2^I) atom] and −0.317(1) Å (Ca atom), respectively. The mean deviation from the plane is 0.232(1) Å. The O(6) oxygen atom is located on the single apex of the bipyramid, O(1) and O(8) oxygen atoms constitute the two apices. The atoms forming the hetero ring of the ligand are almost coplanar, with deviation from the mean plane amounting to 0.017 Å. The planes of the carboxylate groups [C(7),O(1),O(2)] and [C(8),O(3),O(4)] form dihedral angles with the ring plane of 12.1° and 57.4° respectively. The bond lengths and angles within the ligand are in fair agreement with those reported for the parent acid [8]. The Ca–O(carboxylate) interaction modes, Ca coordination scheme, and the range of Ca–O bond lengths agree well with those most frequently observed in a large number of Ca(II) complexes with carboxylate ligands [9].

An interesting feature of the structure is an intramolecular, short and asymmetrical hydrogen bond of 2.378(2) Å, linking the nonbonded oxygen atoms belonging to the second carboxylate groups of the same ligand. The O(2)–H(21) and H(21)–O(4) distances are 1.15(1) and 1.23(1) Å, respectively. The hydrogen atom [H(21)] involved in this bond, readily observed on the Fourier maps, maintains the charge balance within the crystal. The other, weaker, hydrogen bonds link the coordinated water oxygen atoms with carboxylate oxygen atoms belonging to adjacent ribbons. They are listed in detail in Table II.

A different molecular pattern was observed in the structure of Ca(2,3-PZDC)$(H_2O)_2$ dihydrate which was obtained by reacting the parent acid with calcium carbonate [5]. In its structure, the 2,3-PZDC ligand molecule bridges adjacent Ca(II) atoms; however, only one N,O bonding moiety is used. Both oxygen atoms of the second carboxylate group are bonded to an adjacent Ca(II) forming a molecular chain. In addition, they also coordinate Ca(II) atoms belonging to two different neighboring chains forming two-dimensional molecular sheets. This molecular pattern is broken when fairly large chloride anions are accommodated in the crystal as a result of using calcium chloride for chemical synthesis. Catenated polycationic assemblies are formed with a different bridging mode as compared to the "neutral" compound reported [5] and with chloride anions in the interstitial space of the crystal. A similar effect has recently been observed in an another Ca(II) complex which apart from 2,3-PZDC and water ligands also contains nitrate anions [10]. It also seems interesting to note that in the known structures of three Ca(II) complexes with the pyrazine-2,6-dicarboxylate ligand [3,4] dimeric assemblies composed of two Ca(II) ions bridged by two carboxylate oxygens each donated by a different ligand molecule are observed. The dimers are bridged by coordinated water molecules and form molecular ribbons. This molecular pattern appears independently of the procedure for chemical preparation. The structures differ in the amount of solvation water molecules in the interstitial space. One of them also contains a molecule of the parent acid [4].

Supplementary Data

Observed and calculated structure factors and anisotropic thermal parameters can be obtained from the authors on request. Detailed data on the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre under the code number CCDC 234183.

References

[1] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **55**, 1147 (2002) and references therein.
[2] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **56**, 33 (2003) and references therein.
[3] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **56**, 677 (2003).
[4] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **57**, 167 (2004).

[5] H. Ptasiewicz-Bąk and J. Leciejewicz, *Polish J. Chem.* **71**, 1603 (1997).
[6] G.M. Sheldrick, *Acta Crystallogr.* **A46**, 467 (1990).
[7] G.M. Sheldrick, *SHELXL97*, *Program for Crystal Structure Refinement*. (University of Göttingen, Göttingen, 1997).
[8] F. Takusagawa and A. Shimada, *Chem. Lett.* 1121 (1973).
[9] H. Einspahr and C.E. Bugg, *Acta Crystallogr.* **B37**, 1044 (1981).
[10] W. Starosta and J. Leciejewicz, *J. Coord. Chem.* (submitted).