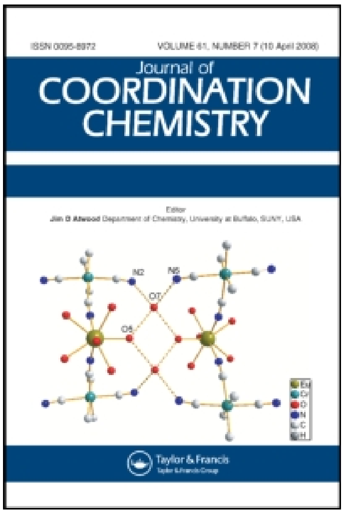

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THE CRYSTAL STRUCTURE OF A STRONTIUM(II) COMPLEX WITH PYRAZINE-2,6-DICARBOXYLATE AND WATER LIGANDS

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Crystals of *catena*-tetraqua{[hexaquabis(μ-pyrazine-2,6-dicarboxylato-O,O')distrontium(II)][tetraquabis-(μ-pyrazine-2,6-dicarboxylato-O,O')distrontium(II)]}trihydrate are triclinic, space group $P\bar{1}$. Two types of symmetry independent dimeric structural units, each composed of two Sr(II) ions, two ligand molecules and water molecules, are bridged by a pair of water molecules which simultaneously are coordinated to the metal ions in the adjacent dimers. In both types of the dimers the Sr(II) ions are bridged by two carboxylate oxygen atoms, each bidentate, donated by a different ligand. The metal ion is also coordinated by one hetero ring nitrogen atom, one carboxylate oxygen atom and five water molecules in one dimer and two water molecules in the other. Two of the water molecules attached to each Sr(II) ion are bridging the dimers into an infinite molecular ribbon. The coordination numbers of the Sr(II) ions in the first and second type dimers are nine and eight, respectively. Solvation water molecules, the coordinated water molecules and the carboxylate oxygen atoms take part in an extended system of hydrogen bonds.

Keywords: Strontium complexes; Pyrazine-2,6-dicarboxylic acid; X-ray crystal structure analysis

INTRODUCTION

Polymeric molecular patterns with different bridging modes have been observed in strontium(II) complexes with pyrazine-2,3-dicarboxylate (2,3-PZDC) and pyrazine-2,5-dicarboxylate (2,5-PZDC) ligands. Two bridging paths were detected in the complex with 2,3-PZDC. None of the complexes coordinate the water oxygen atoms bonded to the Sr(II) ion [1]. On the other hand, water oxygen atoms participate in bridging the Sr(II) ions in the structure of the complex with the 2,5-PZDC ligand, giving rise to a complicated, three-dimensional molecular framework [2].

In this article we report the results of an X-ray diffraction study of the crystal structure of a strontium complex with the pyrazine-2,6-dicarboxylate ligand.

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EXPERIMENTAL

The title compound was obtained in hot aqueous solution by reacting 1 mmol of pyrazine-2,6-dicarboxylic acid dihydrate with 1 mmol of strontium nitrate tetrahydrate. The solution was boiled for 1 h and left at room temperature. Colorless, rectangular single crystals were found in the mother liquid after a couple of days. The dimensions of the crystal used for data collection are given in Table I, together with other details of the experiment. X-ray reflections were measured at room temperature using a KUMA KM4 (Mo-Kα radiation) four circle diffractometer operating in ω–2θ mode. Two standard reflections were measured every 200 reflections. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections ($20^\circ < 2\theta < 30^\circ$). Reflections were processed using profile analysis and corrected for Lorentz factor and polarization effects. An empirical absorption correction based on ψ-scan was applied. Strontium and the coordinated oxygen atoms were located by Patterson synthesis using the SHELXLS program [3]. The remaining atoms including hydrogen were found by successive Fourier syntheses. Final refinement by the least squares method on a set of all unique reflections was done on positional parameters of all atoms, anisotropic temperature factors of all non-H-atoms and isotropic

TABLE I Crystal data and structure refinement details for $Sr_2(2,6\text{-}PZDC)_2(H_2O)_7 \cdot 1.5\,H_2O$

Empirical formula	$C_{12}H_{21}N_4O_{16.5}Sr_2$
Formula weight	660.57
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 12.140(2)$ Å
	$b = 10.085(2)$ Å
	$c = 9.731(2)$ Å
	$\alpha = 87.90(3)^\circ$
	$\beta = 69.20(3)^\circ$
	$\gamma = 82.29(3)^\circ$
	$V = 1103.6$ Å^3
Z	2
Calculated density	1.99 g cm^{-3}
μ (Mo-Kα)	4.92 mm^{-1}
F (000)	658.2
Crystal size	$(0.2 \times 0.2 \times 0.4)$ mm^3
Max 2θ for data collection	58.19°
Index range	$-16 \leq h \leq 5,\ -13 \leq k \leq 13,\ -13 \leq l \leq 12.$
No. of measured reflections	4849
No. of reflections with $F_o > 4\sigma(F_o)$	3658
R_{int}	0.0274
Method of structure solution	Patterson synthesis
Method of structure refinement	full-matrix least squares on F^2
No. of parameters refined	367
Goodness-of-fit on F^2	1.051
Final $R1$ $[F_o > 4\sigma(F_o)]$	0.0336
Final $wR2$ index	0.0943
Absorption correction	ψ-scan
Min. and max. transmission factors	0.875, 0.939
Largest different peak and hole	0.93 and -0.63 e/Å^3
Weight parameters (A,B)	0.0573, 1.55
Mean shift/esd	0.092

temperature factors of hydrogen atoms. A weighting scheme was used in the form: $w = 1/[\sigma^2(F_{\circ}^2) + (A^*P)^2 + B^*P]$, where $P = [\mathrm{Max}(F_{\circ}^2, 0) + 2F_c^2]/3$. A, B are parameters listed in Table I. Calculations were carried out using the SHELXL97 program [4]. Selected bond lengths and angles are listed in Table II. Listings of the observed and

TABLE II Selected interatomic distances (in Å) and angles (in deg.) for $Sr_2(2,6\text{-}PZDC)_2(H_2O)_7 \cdot 1.5\,H_2O$

Strontium coordination:			
Sr1–O11	2.663(3)	O11–Sr1–O11^{I}	70.4(1)
Sr1–O11^{I}	2.679(3)	Sr1–O11–Sr1^{I}	109.6(1)
Sr1–O1	2.703(3)	O1–Sr1–O2	65.2(1)
Sr1–O2	2.677(3)	Sr1–O1–Sr2	114.4(1)
		Sr1–O2–Sr2	114.4(1)
Sr1–N11	2.715(3)		
Sr1–O13	2.621(3)		
Sr1–O3	2.768(4)		
Sr1–O4	2.638(4)		
Sr1–O5	2.623(3)	O21–Sr2–O23	163.7(1)
		O23–Sr2–N21	61.7(1)
Sr2–O21	2.552(3)	N21–Sr2–O21^{II}	61.0(1)
Sr2–O21^{II}	2.652(3)	O21–Sr2–O21^{II}	72.8(1)
Sr2–O1	2.626(3)	Sr2–O21–Sr2^{II}	107.2(1)
Sr2–O2	2.615(3)	O1–Sr2–O2	67.2(1)
		O6–Sr2–O21	94.4(2)
Sr2–N21	2.637(3)	O6–Sr2–O23	94.8(2)
Sr2–O23	2.590(3)	O6–Sr2–O7	69.4(1)
Sr2–O6	2.529(4)	O1–Sr2–O21	85.2(1)
Sr2–O7	2.609(4)	O1–Sr2–O23	94.2(1)
Water molecules:			
O1–H1A	0.64(4)	H1A–O1–H1B	108(2)
O1–H1B	0.64(4)		
O2–H2A	0.72(4)	H2A–O2–H2B	108(2)
O2–H2B	0.72(4)		
O3–H3A	0.81(5)	H3A–O3–H3B	120(4)
O3–H3B	0.81(5)		
O4–H4A	0.64(6)	H4A–O4–H4B	70(9)
O4–H4B	0.67(5)		
O5–H5A	0.53(5)	H5A–O5–H5B	120(6)
O5–H5B	0.53(5)		
O6–H6A	0.68(5)	H6A–O6–H6B	126(4)
O6–H6B	0.68(5)		
O7–H7A	0.66(6)	H7A–O7–H7B	101(9)
O7–H7B	0.66(6)		
O8–H8A	0.64(4)	H8A–O8–H8B	113(1)
O8–H8B	0.85(4)		
O9–H9A	0.86(4)	H9A–O9–H9B	106(2)
O9–H9B	0.46(4)		
Hydrogen bonds:			
D–H···A	D···A	H···A	D–H–A
O1–H1A···O12	2.661(5)	2.12(3)	144(3)
O1–H1B···O9	2.780(8)	2.23(3)	142(1)
O2–H2A···O22	2.728(4)	2.06(3)	153(3)
O2–H2B···O3^{I}	2.822(5)	2.14(4)	158(2)
O3–H3A···O8	2.773(5)	2.04(5)	151(4)
O3–H3B···O24^{III}	2.848(5)	2.06(5)	163(4)
O4–H4A···O14^{IV}	2.967(5)	2.39(6)	149(6)
O4–H4B···N12^{VIII}	2.955(5)	2.31(5)	163(6)
O5–H5A···O23^{III}	2.799(5)	2.44(7)	128(9)

(*continued*)

TABLE II Continued

Hydrogen bonds:			
O5–H5B···O23^{I}	2.876(6)	2.35(7)	170(10)
O6–H6A···O13^{VI}	3.103(6)	2.45(5)	159(4)
O6–H6B···O13^{II}	2.721(6)	2.12(5)	148(4)
O7–H7A···N22^{V}	2.833(5)	2.27(7)	156(6)
O7–O7B···O5^{VI}	2.918(6)	2.48(6)	131(7)
O8–H81···O22^{I}	2.945(5)	2.37(3)	151(1)
O8–H82···O12^{VII}	2.775(5)	1.94(4)	170(9)
O9–H91···O14^{IV}	2.801(8)	1.95(1)	171(2)
O9–H92···O6^{II}	3.009(9)	2.60(4)	149(7)

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

calculated structure factors and anisotropic thermal parameters can be obtained on request from the authors.

DISCUSSION

The structure of the title compound is composed of centrosymmetric dimeric units consisting of two Sr(II) ions, two 2,6-PZDC ligands and water molecules. These Sr(II) ions are bridged by the carboxylate oxygen atoms donated by both ligand molecules. The adjacent dimers are symmetry independent and differ in the number of coordinated water molecules to the metal ion. Two Sr(II) ions belonging to adjacent dimers are bridged by a pair of coordinated water molecules forming an infinite molecular ribbon. Figure 1 shows a fragment of the ribbon with numbering of atoms; Fig. 2 – the packing of ribbons.

The bridging of two Sr(II) ions in a dimer is accomplished by two carboxylate oxygen atoms, each donated by a separate ligand molecule. These atoms are bidentate since they are simultaneously coordinated to both metal ions in the dimer. The other oxygen atom in each of these bridging carboxylate groups does not take part in bonding. The 2,6-PZDC ligand molecule acts in the tridentate mode, since, apart from the bridging carboxylate oxygen atom it contributes to metal ion coordination one nitrogen atom of the diazine ring and one oxygen atom from the other carboxylate group leaving its second oxygen atom unbonded. The Sr1 ion and the diazine rings of the ligand are almost planar, however, the bridging carboxylate group deviates strongly from the mean plane by 1.348(7), 1.267(6) and 1.331(6) Å in the case of C17, O11 and O12 atoms, respectively. On the other hand, in the second carboxylate group, the C18, O13 and O14 atoms show only small deviations from the mean plane (less than 0.02 Å). In the case of the other dimer which contains the Sr2 ions, the metal ion and the diazine ring are also coplanar, but both carboxylate groups show distinct displacements from the mean plane: -0.540 Å in the case of the C27, O21 and O22 atoms and $+0.227$ Å for the C28, O23 and O24 atoms.

Five water molecules complete the coordination number to nine in the case of the Sr1 ion and four water molecules to eight in the case of the Sr2 ion. Two of the water molecules are bridging the dimers, giving rise to molecular ribbons which are the characteristic motif of the structure of the title compound. The coordination polyhe-

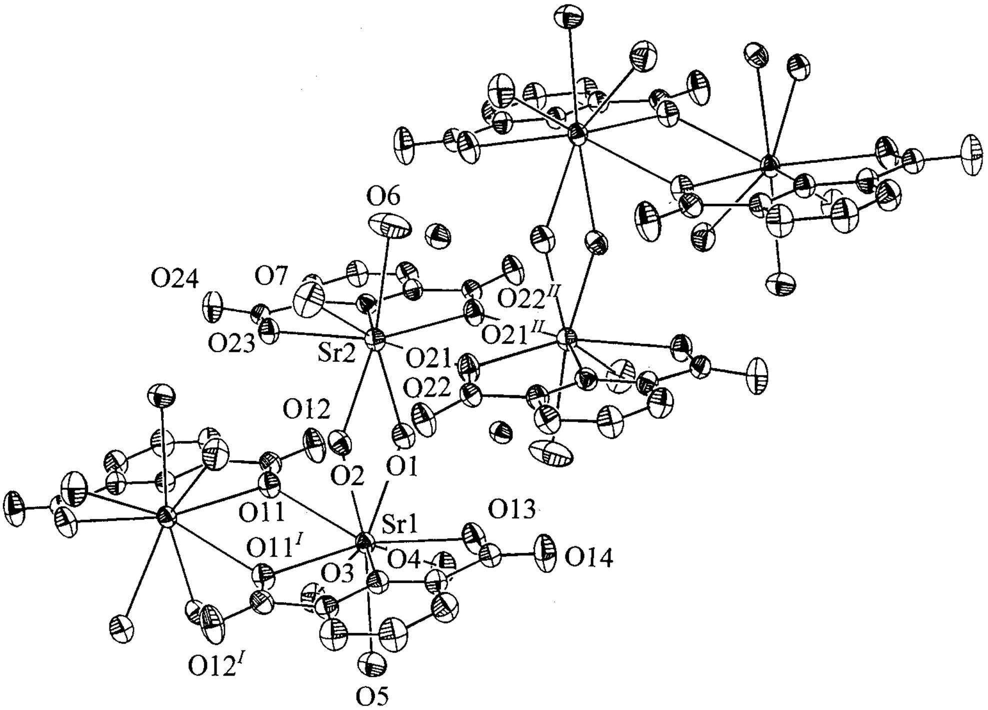

FIGURE 1 A fragment of the molecular ribbon in $Sr_2(2,6\text{-}PZDC)_2(H_2O)_7 \cdot 1.5\ H_2O$ with the numbering of strontium and oxygen atoms. For clarity of the picture, the other atoms are not marked. The nonhydrogen atoms are shown as 50% probability ellipsoids.

dron around the Sr1 ion has nine apices constituted by one diazine ring nitrogen atom, three carboxylate oxygen atoms and five water oxygen atoms. A highly distorted equatorial plane can be visualized as consisting of the Sr1, N11, O11, O13, O3 and O4 atoms with maximum shifts from the mean plane amounting to $+0.990(3)$ Å (the O11 atom) and $-1.103(3)$ Å (the O3 atom). The O1 and O2 atoms form the apices on one side of this plane and O11^{I} and O5 atoms on the other. Thus, a bicapped, strongly distorted pentagonal bipyramid can be imagined as the coordination polyhedron of the Sr1 ion. A bicapped bipyramid with the equatorial plane formed by the Sr2, N21, O21, O21^{II} and O23 atoms and the bridging O1 and O2 water oxygen atoms constituting the apices on one side and O6 and O7 water oxygen atoms on the other, can be visualized as the coordination polyhedron around the Sr2 ion. The equatorial plane in the form of a strongly distorted tetragon is almost planar: maximum deviations from the mean plane are $+0.074(3)$ Å (the Sr2 atom) and $-0.060(3)$ Å (the N21 atom). The respective bond distances and angles are listed in detail in Table II. The observed Sr–O bond lengths in the title compound are in the same range as, for example, those detected previously in the strontium complexes with pyrazine dicarboxylate ligands [1,2] and strontium dipicolinate tetrahydrate [5]. Also the bond lengths and angles within both symmetry independent ligand molecules agree fairly well with those reported for the pyrazine-2,3-dicarboxylate and pyrazine-2,5-dicarboxylate analog [1,2].

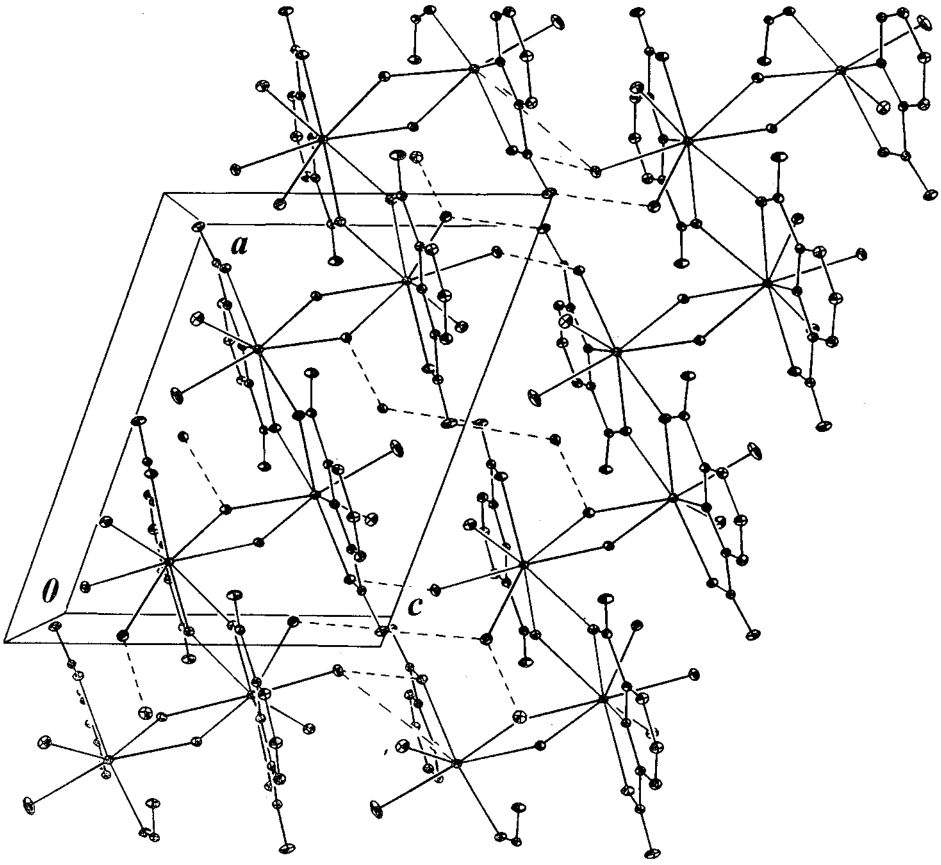

FIGURE 2 The packing of the molecular ribbons in the structure of $Sr_2(2,6\text{-}PZDC)_2(H_2O)_7 \cdot 1.5H_2O$. Hydrogen bonds are marked by dashed lines.

Solvation water molecules have been found in the structure. One of them was refined with an occupation factor of 0.5.

All the water molecules participate in an extended network of hydrogen bonds. For example, the bridging water molecules O1 and O2 are linked to the 'free' carboxylate oxygen atoms O12 and O22 by fairly short hydrogen bonds of 2.727 and 2.658 Å, respectively. All the hydrogen bonds operating in the structure are listed in Table II.

The molecular pattern and the bridging modes observed in the title compound are entirely different from those detected previously in the Sr(II) complexes with the 2,3-PZDC and 2,5-PZDC ligands. The structure of the former consists of molecular sheets in which two bridging paths can be distinguished. In the first, two Sr(II) ions are bridged by the ligand molecule which contributes one oxygen atom of a carboxylate group and the nearest hetero ring nitrogen atom (the N,O bonding moiety) for coordination, while the other Sr(II) ion is coordinated by both oxygen atoms of the second carboxylate group leaving the nearest nitrogen atom inactive. Molecular chains can thus be visualized, however, both carboxylate atoms act in the bidentate mode and are coordinated to the metal ions in adjacent chains constituting the second bridging path and forming two-dimensional molecular sheets. Three coordinated water molecules per Sr(II) ion do not participate in the bridging system [1].

In the structure of the Sr(II) complex with the 2,5-PZDC and water ligands two metal ions are bridged by a 2,5-PZDC ligand which uses both is N,O bonding moieties forming a molecular chain. However, this oxygen atom is bidenate and interacts with a metal ion in the adjacent chain. In addition two Sr(II) ions in the adjacent chains are bridged by a pair of coordinated water oxygen atoms, each donated by different metal coordination sphere giving rise to a complicated three-dimensional molecular framework [2].

It may be interesting to note that the structure of the Sr(II) complex with the pyridine-2,6-dicarboxylate (dipicolinate) and water ligands contains neither dimeric units nor bridging via water oxygen atoms. This structure is built up from molecular ribbons composed of metal ions bridged by carboxylate oxygen atoms of the bidentate dipicolinate ligands. The coordinated water molecules do not participate in the bridging system [5].

Single dimeric structural units of the same type as observed in the title compound have been discovered in a Ca(II) complex with pyridine-2,6-dicarboxylate and water ligands [6] and a Ca(II) complex with pyridine-3,5-dicarboxylate and water ligands [7]. Dimeric units, but bridged by a pair of water oxygen atoms to form molecular ribbons of the same kind as observed in the title compound, constitute the molecular patterns discovered in the structures of two Ca(II) dipicolinates [8,9] and two Ca(II) complexes with pyrazine-2,6-dicarboxylate and water ligands [10].

The observation in the title compound that only the diazine nitrogen atom located in the neighborhood of the carboxylic groups takes part in chelating the metal ion, the other nitrogen atom being inactive in coordination, supports the hypothesis that the carboxylic group activates the hetero ring nitrogen atom to coordinate the metal ion. This effect is clearly visible in the structure of the Sr(II) complex with the 2,5-PZDC ligand in which both N, O bonding moieties are active in bridging adjacent metal ions.

References

[1] H. Ptasiewicz-Bąk and J. Leciejewicz, *Polish J. Chem.* **72**, 627 (1998).
[2] H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **44**, 237 (1998).
[3] G.M. Sheldrick, *Acta Cryst.* **A46** 467 (1990).
[4] G.M. Sheldrick, Program for crystal structure refinement. (University of Göttingen, Germany, 1997).
[5] K.J. Palmer, R.Y. Wong and J.C. Lewis, *Acta Cryst.* **B28**, 223 (1972).
[6] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **55**, 469 (2002).
[7] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz, *J. Coord. Chem.* **55**, 1 (2002).
[8] G. Strahs and R.E. Dickerson, *Acta Cryst.* **B24**, 571 (1968).
[9] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz. *J. Coord. Chem.* **55**, 1147 (2002).
[10] W. Starosta, H. Ptasiewicz-Bąk and J. Leciejewicz. *J. Coord. Chem.* (in press).