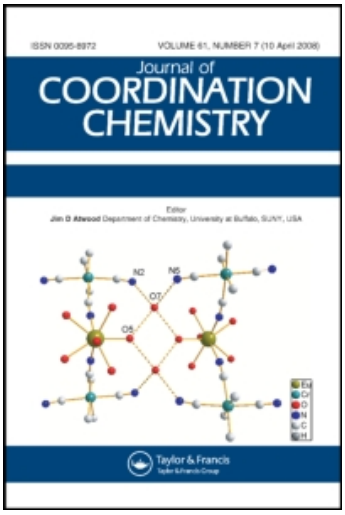

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STRONTIUM IONS BRIDGED BY PYRAZINE-2,5-DICARBOXYLIC ACID AND WATER MOLECULES MAKE A THREE-DIMENSIONAL POLYMERIC STRUCTURE OF TRIAQUOMONO (μ-PYRAZINE-2,5-DICARBOXYLATO) STRONTIUM(II) DIHYDRATE CRYSTALS

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Triaquo(μ-pyrazine-2,5-dicarboxylato)strontium(II) dihydrate, $SrC_6H_{12}N_2O_9$ crystallizes in the triclinic system, space group $P\bar{1}$, $a = 6.238(1)$ Å, $b = 9.418(2)$ Å, $c = 10.591(2)$ Å, $\alpha = 73.58(3)°$, $\beta = 80.52(3)°$, $\gamma = 75.01(3)°$, $Z = 2$. The structure is polymeric. Strontium ions are bridged by pyrazine-2,5-dicarboxylic acid molecules which use both (N,O)-bonding moieties (mean Sr–O = 2.567(3) Å, mean Sr–N = 2.826(3) Å). In addition, the bridging is accomplished by two oxygen atoms from water molecules (mean Sr–O = 2.681(3) Å) and bidentate oxygen atoms (Sr–O = 2.697(3) Å) from a carboxylic group of a pyrazine-2,5-dicarboxylic acid molecule. As a result, a three-dimensional molecular framework is formed. The coordination around the Sr ion is ninefold: seven oxygen and two nitrogen atoms make a distorted, monocapped square antiprism. Two water molecules per unit cell are situated in the holes of this framework and participate in an extended hydrogen bond scheme.

Keywords: Strontium complexes; pyrazine-2,5-dicarboxylic acid; X-ray crystal structure analysis

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INTRODUCTION

Divalent metal complexes with pyrazine-2,3-dicarboxylic acid (2,3-pzdc) exhibit polymeric structures in which metal ions are bridged either *via* both (N, O)-bonding moieties or *via* only one (N, O)-bonding moiety and an oxygen atom of the second carboxylic group. The latter is usually bridging. For example, the magnesium complex shows a polymeric structure consisting of Mg ions bridged by 2,3-pzdc molecules *via* one (N, O)-bonding moiety and the bridging second carboxylic group forming molecular ribbons.[1] On the other hand, the structure of the magnesium complex with pyrazine-2,5-dicarboxylic acid (2,5-pzdc) contains $Mg(H_2O)_6^{+2}$ cations and $(2,5\text{-pzdc})^{-2}$ anions held together by strong hydrogen bonds between the water molecules and carboxylic oxygens.[2] It therefore seemed interesting to find how the different configuration of carboxylic groups present in 2,5-pzdc will influence the molecular framework in the calcium and strontium complexes as compared to the respective compounds of 2,3-pzdc which show complex polymeric structures.[3,4] The results of a X-ray crystal structure of the strontium complex with 2,5-pzdc are reported in this paper.

EXPERIMENTAL

The title compound was synthesized by reacting 1 mmol of 2,5-pzdc (Across Chimica) dissolved in 10 mL of hot water with 1 mmol of strontium carbonate. After the $SrCO_3$ was dissolved, the solution was boiled for 1 h. Colorless single crystals in the form of prismatic plates appeared overnight in the mother liquid. They were washed with cold water. The dimensions of a single crystal selected for X-ray data collection are listed in Table I.

The reflections were measured at room temperature using a KUMA KM4 (CuK_α radiation) four-circle diffractometer operating in $\omega - 2\theta$ mode. Scan-range was +0.65 (ω) around $K_{\alpha 1}$–$K_{\alpha 2}$ angles, scan speed 5–15(ω) min^{-1} depending on the intensity of a pre-scan; backgrounds were measured at each end of the scan for 0.3 of the scan time. Two standard reflections were monitored every 200 reflections. They remained constant throughout every data collection process. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections ($18° < 2\theta < 38°$). Reflections were processed using profile analysis in each case and were corrected for Lorentz factor and polarization effects, those with $I/\sigma(I) > 4.0$ where used in the refinement. No absorption correction was applied. Non-hydrogen ions were located by direct methods using the SHELXLS program.[5]

TABLE I Crystal data and structure refinement details for $Sr(2,5\text{-pzdc})(H_2O)_3.2H_2O$

Empirical formula	$Sr\ C_6H_{12}N_2O_9$
Formula weight	343.8
Temperature	293 K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 6.238(1)$ Å $b = 9.418(2)$ Å $c = 10.591(2)$ Å $\alpha = 73.58(3)°$ $\beta = 80.52(3)°$ $\gamma = 75.01(3)°$
Volume	573.7 Å^3
Z	2
Density (calculated)	1.99 g cm^{-3}
μ (CuKα)	7.02 mm^{-1}
$F(000)$	344.0
Crystal size	$0.20 \times 0.10 \times 0.05$ mm^3
θ range for data collection	83°
Index ranges	$-7 < h < 0, -12 < k < 11,$ $-13 < l < 13$
No. of reflections collected	2171
No. of independent reflections	1986
R_{int}	0.054
Method of structure solution	Direct method
Method of structure refinement	Full-matrix least squares on F^2
No. of parameters refined	213
Data/parameters/restrains	None
Data/parameters ratio	9.32
Goodness-of-fit on F^2	1.113
Final $R1$ index	0.036
Final $wR2$ index	0.091
Absorption parameters	None
Largest diff. peak and hole	1.31 e/Å^3, −1.61 e/Å^3
Weight parameters (A, B)	0.0726, 0.0
Mean Shift/e.s.d.	0.009

Hydrogen atoms were found by difference Fourier syntheses. Final refinement was done on positional parameters of all atoms and anisotropic temperature factors for all non-H-atoms and isotropic temperature factors for hydrogen atoms. Final refinement was on F^2 by least-squares methods. A weighting scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (A * P)^2 + B * P]$, where $P = (\mathrm{Max}(F_o^2) + 2F_c^2)/3$ and A, B are refined parameters listed in Table I. Computing was carried out with SHELXL 93.[6] Final atomic coordinates and equivalent isotropic displacements are shown in Table II, selected bond lengths and angles in Table III. Listings of calculated and observed structure factors and anisotropic thermal parameters can be obtained from the authors on request.

TABLE II Fractional atomic coordinates and equivalent isotropic displacement ($Å^2$) for $Sr(2,5\text{-pzdc})(H_2O)_3 \cdot 2H_2O$

Atom	*x*	*y*	*z*	*Ueq*
Sr	0.26298(5)	0.89470(3)	0.64012(3)	0.0184(1)
O1	−0.0347(5)	0.7394(4)	0.7293(3)	0.029(1)
O2	0.471(1)	0.6841(7)	0.8239(8)	0.064(1)
O3	0.1453(5)	0.9245(3)	0.4017(3)	0.022(1)
O4	0.0540(8)	0.4447(5)	0.8900(4)	0.045(1)
(1/2)O51	0.268(1)	0.6223(7)	0.2124(7)	0.034(1)
(1/2)O52	0.355(1)	0.6141(8)	0.0856(8)	0.048(1)
O11	0.6518(5)	0.8406(3)	0.5147(3)	0.024(1)
O12	0.9200(5)	0.7163(3)	0.3917(3)	0.029(1)
C13	0.6951(6)	0.4860(4)	0.4278(3)	0.022(1)
C12	0.6099(6)	0.6090(4)	0.4831(3)	0.016(1)
C11	0.7380(5)	0.7317(4)	0.4616(4)	0.018(1)
N1	0.5870(5)	0.3769(4)	0.4439(3)	0.022(1)
O21	0.5252(6)	0.9739(4)	0.2400(3)	0.030(1)
O22	0.5631(6)	0.8007(4)	0.1269(4)	0.042(1)
C23	1.1013(6)	1.0783(4)	0.0481(4)	0.021(1)
C22	0.8221(5)	0.9557(4)	0.0725(3)	0.018(1)
C21	0.6184(5)	0.9059(4)	0.1544(3)	0.024(1)
N2	0.9231(5)	1.0349(3)	0.1211(3)	0.019(1)
H1	0.83(1)	0.48(1)	0.36(1)	0.03(1)
H2	1.17(1)	1.14(1)	0.07(1)	0.07(2)
H11	−0.00(1)	0.64(1)	0.77(1)	0.04(1)
H12	−0.14(1)	0.76(1)	0.70(1)	0.04(1)
H21	0.40(1)	0.68(1)	0.87(1)	0.01(1)
H22	0.43(2)	0.62(1)	0.83(1)	0.11(5)
H31	0.26(1)	0.94(1)	0.34(1)	0.01(1)
H32	0.12(1)	0.87(1)	0.39(1)	0.02(1)
H41	0.20(1)	0.36(1)	0.88(1)	0.09(3)
H42	0.06(3)	0.41(2)	0.92(2)	0.028(10)

DISCUSSION

The structure of the title compound can be visualized as a three-dimensional molecular framework in which Sr ions are linked by 2,5-pzdc and water molecules. The two symmetry related Sr ions in the unit cell are bridged by the 2,5-pzdc molecule (a), which uses both its N, O-bonding moieties with typical Sr–N and Sr–O bonds of 2.826(3) and 2.567(3) Å respectively. This bridging 2,5-pzdc molecule has its center at 1/2, 1/2, 1/2 and is planar with maximum out-of-plane shift of 0.001(9) Å (see Figure 1). The planes of both carboxylic groups make dihedral angles of only 0.9(1)° with the plane of the pyrazine ring. Only one oxygen of each carboxylic group is used for bonding, the other one is inactive. The bonding oxygen acts as bridging since apart from taking part in the N, O-bonding moiety it is simultaneously chelated to another Sr ion which is situated in the neighboring unit cell. (see Figure 2) with a Sr–O bond distance of 2.697 Å.

TABLE III Selected interatomic distances (in Å) and angles (in deg.) for Sr(2,5-pzdc) $(H_2O)_3 \cdot 2\,H_2O$

(a) *Covalent bonds*:			
Sr–O11	2.567(3)	O11–Sr–O11^{III}	71.3(1)
Sr–O11^{III}	2.697(3)	O11–Sr–O21^{III}	81.1(3)
Sr–O21^{III}	2.678(3)	O11–Sr–N1^{I}	60.6(1)
Sr–N1^{I}	2.826(3)	O11–Sr–N2^{III}	137.7(1)
Sr–N2^{III}	2.786(3)	O11–Sr–O1	133.2(1)
Sr–O1	2.555(3)	O11–Sr–O2	80.5(2)
Sr–O2	2.595(5)	O11–Sr–O3	80.6(1)
Sr–O3	2.663(3)	O11–Sr–O3^{II}	139.2(1)
Sr–O3^{II}	2.699(3)	O11^{III}–Sr–O21^{III}	67.2(1)
O11^{III}–Sr–N1^{I}	121.1(1)	O3–Sr–O3^{II}	66.9(1)
O11^{III}–Sr–N2^{III}	103.6(1)	N1^{I}–Sr–O1	72.8(1)
O11^{III}–Sr–O1	145.1(1)	N1^{I}–Sr–O2	71.0(2)
O11^{III}–Sr–O2	132.9(2)	N1^{I}–Sr–O3	67.6(1)
O11^{III}–Sr–O3	73.1(1)	N1^{I}–Sr–O3^{II}	122.1(1)
O11^{III}–Sr–O3^{II}	76.0(1)	N2^{III}–Sr–O1	74.7(1)
O21^{III}–Sr–N1^{I}	130.0(1)	N2^{III}–Sr–O2	73.4(1)
O21^{III}–Sr–N2^{III}	59.6(1)	N2^{III}–Sr–O3	139.6(1)
O21^{III}–Sr–O1	131.5(1)	N2^{III}–Sr–O3^{II}	73.2(1)
O21^{III}–Sr–O2	71.9(2)	O1–Sr–O2	80.8(2)
O21^{III}–Sr–O3	139.8(1)	O1–Sr–O3	85.9(1)
O21^{III}–Sr–O3^{II}	108.0(1)	O1–Sr–O3^{II}	70.1(1)
O2–Sr–O3	138.6(2)	O2–Sr–O3^{II}	140.3(2)
N1–C12^{I}	1.336(4)	C12^{I}–N1–C13	116.4(3)
N1–C13	1.328(4)	N1–C13–C12	122.4(3)
C13–C12	1.389(5)	N1^{I}–C12–C13	121.2(3)
C11–C12	1.515(4)	O12^{I}–C11–O11	125.8(3)
C11–O11	1.263(4)		
C11–O12	1.248(4)		
N2–C22	1.337(4)	C22–N2–C23	116.7(3)
N2–C23	1.331(4)	N2–C23–C22^{IV}	121.9(3)
C23–C22^{IV}	1.384(5)	N2–C22–C23^{IV}	121.4(3)
C21–C22	1.517(5)	O22–C21–O21	127.3(3)
C21–O21	1.238(5)		
C21–O22	1.249(5)		
C13–H1	0.98(5)		
C23–H2	1.02(8)		
O1–H11	0.87(7)	H11–O1–H12	114(6)
–H12	0.78(7)		
O2–H21	0.67(6)	H21–O2–H22	98(10)
–H22	0.57(8)		
O3–H31	0.90(5)	H31–O3–H32	102(7)
–H32	0.52(6)		
O4–H41	1.01(10)	H41–O4–H42	69(10)
–H42	0.41(18)		
(b) *Hydrogen bonds*:			
O1.....O4	2.784(6)	O1–H11.....O4	178(6)
H11...O4	1.93(7)		
O1.....O11^{V}	3.028(4)	O1–H12.....O11^{V}	149(6)
H12...O11^{V}	2.33(7)		
O3.....O21	2.747(4)	O3–H31.....O21	171(6)
H31...O21	1.86(5)		
O3.....O12^{V}	2.725(4)	O3–H32.....O12^{V}	156(13)

TABLE III (*Continued*)

H32..O12^{V}	2.23(6)		
O4.....O22^{I}	2.884(5)	O4–H41.....O22^{I}	165(15)
H41...O22^{I}	1.87(12)		
O2^{VI}....(1/2)O52	2.676(11)	O2^{VI}–H21^{VI}..(1/2)O52	143(11)
H21^{VI}..(1/2)O52	2.14(7)		
O2^{I}.....(1/2)O52	2.694(10)	O2^{I}–H22^{I}.....(1/2)O52	140(5)
H22^{I}....(1/2)O52	2.21(9)		
O2^{I}.....(1/2)O51	3.026(8)	O2^{I}–H22^{I}.....(1/2)O51	138(5)
H22^{I}....(1/2)O51	2.56(5)		
O22.....(1/2)O51	2.683(8)		
O12.....(1/2)O51	2.779(9)		
O22.....(1/2)O52	2.601(4)		
O4^{VII}...(1/2)O52	2.704(7)		
O4^{VII}...(1/2)O51	2.719(9)		

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

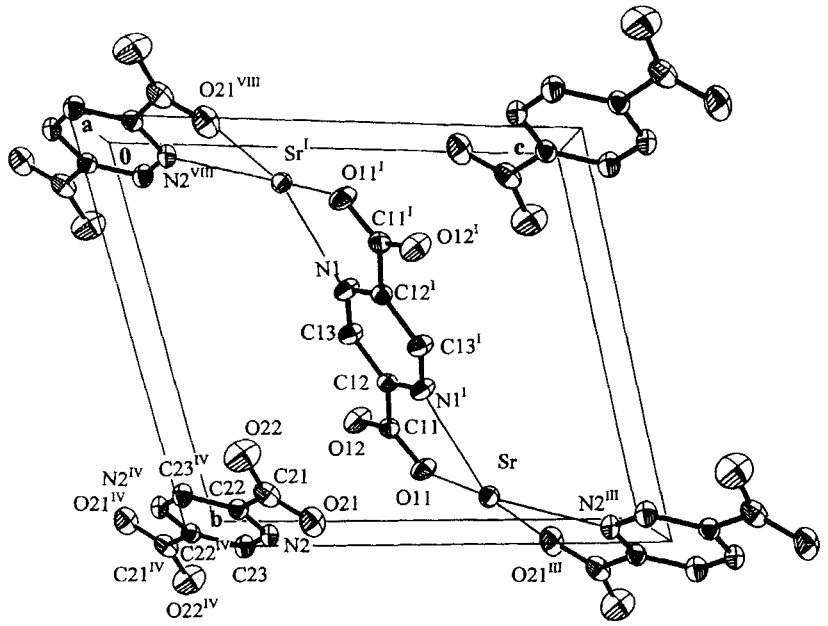

FIGURE 1 A fragment of the chain in the polymeric structure of Sr(2,5-pzdc)$(H_2O)_3 \cdot 2H_2O$. The numbering of atoms refers to Table III. ^{I}: $-x+1, -y+1, -z+1$; ^{II}: $-x, -y+2, -z+1$; ^{III}: $-x+1, -y+2, -z+1$; ^{IV}: $-x+2, -y+2, -z$; ^{V}: $x-1, y, z+1$; ^{VI}: $x, y, z+1$; ^{VII}: $-x, -y+1, -z+1$; ^{VIII}: $x, y-1, z$.

In turn, the bridging oxygen atom form the carboxylic group belonging to the 2,5-pzdc molecule in the neighboring unit cell is linked to the Sr(a)ion with the same bond distance as above. The Sr, O11, Sr^{III} and O11^{III} atoms (see Figure 3) make a plane which is inclined by the angle of 37.8(8)° to the

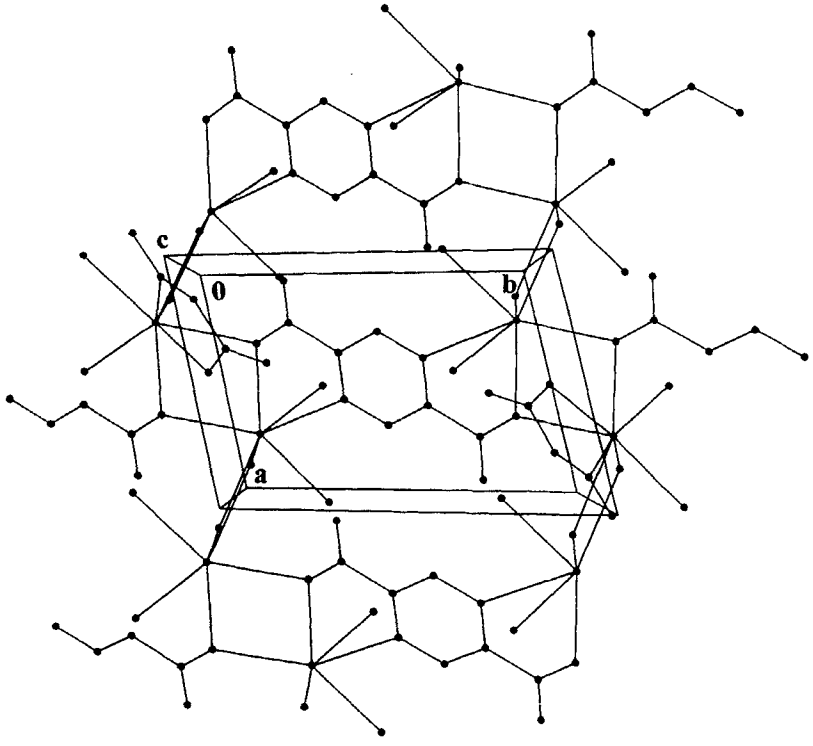

FIGURE 2 Packing diagram of the $Sr(2,5\text{-pzdc})(H_2O)_3 \cdot 2H_2O$ structure. The solvation water molecules are not shown for clarity.

plane of the 2,5-pzdc molecule. This bonding scheme gives rise to molecular ribbons propagating approximately along the [110] direction in the crystal.

There is a second 2,5-pzdc molecule (b) bridging with its center at 0, 0, 0. It links a Sr ion with the other one in the adjacent unit cell using also both its (N, O)-bonding moieties with Sr–N and Sr–O bonds amounting to 2.876(3) and 2.699(3) Å, respectively. However, their carboxylic oxygens remain monodentate (see Figure 1). This 2,5-pzdc molecule is also planar with a maximum out-of-plane shift of 0.002(9) Å. The planes of molecules (a) and (b) make a dihedral angle of 33.4(8)°. The bond lengths and angles within both 2,5-pzdc molecules (Table III) agree fairly well with those reported for the pyrazine-2,5-dicarboxylic acid dihydrate analogue.[2]

Two nearest Sr ions belonging to adjacent ribbons are additionally bridged by oxygen atoms of two water molecules, O3 and $O3^{II}$, with Sr–O bonds of 2.664 and 2.699 Å respectively. In this way, a three-dimensional framework is formed as shown in Figure 3. The two Sr ions and two

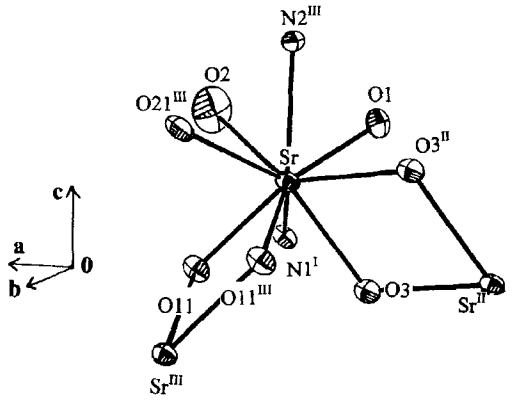

FIGURE 3 The coordination around Sr ion in the structure of $Sr(2,5\text{-pzdc})(H_2O)_3 \cdot 2H_2O$. The nearest Sr ions are bridged by water oxygen O3 and by oxygen from carboxylic group O11. The numbering of atoms refers to Table III.

oxygen atoms constitute a plane with a maximum shift from the best plane of 0.0001(1) Å.

The coordination around the Sr ion is ninefold: apart from two nitrogen atoms, three carboxylate oxygens and two bridging water oxygens there are two more water oxygens coordinated to each Sr ion (see Table III for the respective bond distances and selected angles). The nine atoms coordinated to strontium form a distorted, monocapped square antiprism displayed in Figure 3. This shape has also been found in the structure of the strontium complex with pyridine-2,6-dicarboxylic acid (pda),[7] but is different from that observed in the structure of the strontium complex with pyrazine-2,3-dicarboxylic acid. The coordination of strontium in the latter is also ninefold but has a more complicated shape.[4]

The bridging modes found in the title compound are different from those operating in the $Sr(2,3\text{-pzdc})(H_2O)_3$ crystals where only one (N, O)-bonding moiety of the 2,3-pzdc molecule is bridging while the second carboxylic group uses both its oxygens for bridging leaving its second heteroring nitrogen inactive. The structure consists of two-dimensional sheets with three water oxygens bonded to each Sr ion but not participating in the bridging system.

The Sr–O and N–O bond distances in the title compound are similar to those found in the structures of other strontium complexes with pyridine and pyrazine carboxylic acids. This is illustrated in Table IV.

There are two water molecules per unit cell situated in the holes of the molecular framework constituting the structure of the title compound. One of them occupies two sites with probability of 50%. These water molecules

TABLE IV Mean Sr–N, Sr–$O_{carboxyl}$, Sr–O_{water} bond distances in some strontium complexes (in Å)

Compound	*Coordination*	Sr–N	Sr–$O_{carboxyl}$	Sr–O_{water}	*Ref.*
Sr(2,5-pzdc)$(H_2O)_3 \cdot 2H_2O$	9	2.806	2.647	2.618	This work
Sr(2,3-pzdc)$(H_2O)_3$	9	2.793	2.673	2.665	4
Sr(dpa)$(H_2O)_4$	9	2.640	2.617	2.617	7
Sr$(pzca)_2(H_2O)_4$	8	2.751	2.588	2.573	8

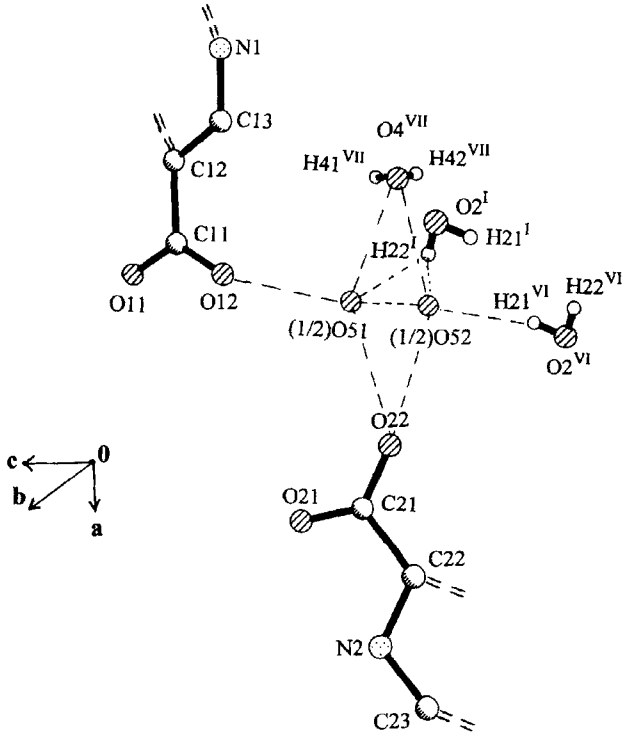

FIGURE 4 The disordered water molecules (1/2)O51 and (1/2)O52 in the hydrogen bond network in the structure of Sr(2,5-pzdc)$(H_2O)_3 \cdot 2H_2O$. The numbering of atoms refers to Table III.

take part in the hydrogen bond network. The "disordered" water molecule (1/2)O51 and (1/2)O52 is active in a hydrogen bond network which links either two "inactive" carboxylic oxygens O22 and O12 of two different 2,5-pzdc molecules (see Figure 4) or an "inactive" carboxylic oxygen O22 with a water molecule O2 coordinated to a Sr ion. However, the "disordered" water molecule interacts also with the second solvation water molecule O4

via fairly strong hydrogen bonds either of 2.704(7) or 2.719(9) Å depending on the occupied site. The O4 solvation water molecule takes part in fairly strong hydrogen bonds of 2.784(6) and 2.884(5) Å to the coordinated water molecule O1 and the "inactive" carboxylic oxygen O22. Also the "bridging" water oxygen O3 forms hydrogen bonds to the carboxylic oxygens O21 and O12. All respective bond distances and angles are listed in Table III.

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