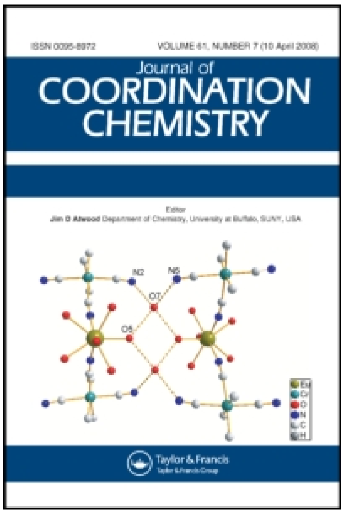

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X-RAY DIFFRACTION STUDY OF THE CRYSTAL STRUCTURES OF PYRAZINE-2,5-DICARBOXYLIC ACID DIHYDRATE AND ITS MAGNESIUM COMPLEX

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Pyrazine-2,5-dicarboxylic acid dihydrate, $C_4H_2N_2(COOH)_2 \cdot 2H_2O$, is triclinic, $P1$, $a = 5.255(1)$ Å, $b = 6.907(1)$ Å, $c = 6.951(1)$ Å, $\alpha = 119.(3)°$, $\beta = 100.81(3)°$, $\gamma = 99.06(3)°$, $Z = 1$. The structure is composed of molecular layers consisting of 2,5-pzdc and water molecules held by a system of hydrogen bonds. The interlayer spacing of 3.2 Å indicates interactions of the van der Waals type.

Magnesium pyrazine-2,5-dicarboxylate hexahydrate, $[Mg(H_2O)_6][C_4H_2N_2(COO)_2]$, is monoclinic, $P2_1/c$, $a = 8.016(1)$ Å, $b = 6.858(1)$ Å, $c = 11.278(1)$ Å, $\beta = 99.52(3)°$, $Z = 2$. Each magnesium atom is surrounded by six water molecules located at the apices of an almost regular octahedron with mean $d_{Mg-O} = 2.060(1)$ Å. The 2,5-pzdc anions are planar with interatomic distances and angles characteristic for the pyrazine ring. A number of hydrogen bonds link the water molecules coordinated to Mg with carboxylic oxygens of the acid molecules. Their lengths range from 2.51 Å to 3.07 Å.

Keywords: Pyrazine-2,5-dicarboxylic acid; magnesium complex; X-ray crystal structure analysis

INTRODUCTION

Polymeric structures with a variety of bonding schemes have been detected in the complexes of pyrazine-2,3-dicarboxylic acid with a number of divalent ions.[1] In all complexes the ring nitrogen and the oxygen of the nearest monodentate carboxylic group were involved in chelating the central ion. However, in some of the complexes the second carboxylic group acting

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either as a monodentate or bidentate ligand are bonded to the metal ion leaving its nearest ring nitrogen inactive.

A polymeric chain structure has been detected in the magnesium complex of pyrazine-2,3-dicarboxylic acid.[1] Therefore, the magnesium compound of the title acid was chosen as the first in our studies of the crystal chemistry of 2,5-pzdc complexes with divalent ions, followed by the structure of the strontium compound.[2] Since the structure of the ligand acid has not been reported, the manuscript also contains the results of an X-ray diffraction study of its crystal and molecular structure.

EXPERIMENTAL

Commercial grade pyrazine-2,5-dicarboxylic acid (Across Chimica) – the title compound (I) – was recrystallized from aqueous solution. Rectangular, colorless single crystals separated overnight. The title compound (II) was synthesized by reacting 0.204 g of 2,5-pzdc dissolved in 10 mL. of hot water with 0.84 g magnesium carbonate. After evaporation at room temperature, rectangular colorless single crystals could be selected. The yield was 83%. The dimensions of the crystals used in the X-ray data collection are given in Table I. The reflections were measured at room temperature using a KUMA KM4 four circle diffractometer operating in the 2Θ–ω mode. Maximum $\sin\Theta/\lambda$ values are shown in Table I. The scan range was $+0.65(\omega)$ around $K_{\alpha 1}$–$K_{\alpha 2}$ angles, and the scan speed 5–$15(\omega)\,\mathrm{min}^{-1}$ depending on the intensity of the pre-scan. 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 a least-squares fit of 24 reflections ($18 < 2\Theta < 30$) deg. Reflections were processed using profile analysis in each case and were corrected for Lorentz factor and polarization effects. No absorption correction was applied. Non-hydrogen atoms were located by the direct method section of SHELXLS[3] and hydrogen atoms then found by successive Fourier syntheses. Final refinement was carried out on positional parameters of all atoms, anisotropic temperature factors for all non-H atoms and isotropic temperature factors for hydrogen atoms. Since the number of reflections with $I/\sigma^2(I) > 4.0$ collected for compound (I) was only 645 but the number of refined parameters 152, all observed reflections with $I/\sigma^2(I) > 1.0$ were used in the refinement process. On the other hand, in the case of compound (II) only the reflections with $I/\sigma^2(I) > 4.0$ were used. Final refinement was on F^2 by the least squares method. A weighting scheme was used in the form

TABLE I Crystal data, X-ray refinement details

Compound	I	II
Formula	$C_6H_8N_2O_6$	$C_6H_{14}N_2O_{10}Mg$
M	204.1	298.3
System	Triclinic	Monoclinic
Systematic Absences	None	h0l(l ≠ 2n), 0k0(k ≠ 2n).
Space group	$P1$	$P2_1/c$
a [Å]	5.255(1)	8.016(2)
b [Å]	6.907(1)	6.858(1)
c [Å]	6.951(1)	11.278(2)
α [deg]	119.72(3)	
β [deg]	100.81(3)	99.52(3)
γ [deg]	99.06(3)	
V [$Å^3$]	205.74	611.46
Z	1	2
D_c [$g cm^{-3}$]	1.647	1.620
$(\sin\theta/\lambda)$max	0.627	0.639
index ranges	−6/6, −7/8, −8/0	0/10, 0/8, −14/14
μ [mm^{-1}]	(Cu-Kα) 1.32	(Cu-Kα) 1.81
Crystal size [mm]	0.20 × 0.10 × 0.05	0.10 × 0.20 × 0.20
refls.unique	(with $I/\delta^2 > 1.0$) 732	(with $I/\delta^2 > 4.0$) 943
R_{int}	0.068	0.026
Parameters refined	152	117
Weight parameters [A,B]	0.11, 0.0	0.06, 0.11
Mean shift/esd	0.099	0.041
Final $R1$	0.049	0.029
Final w$R2$	0.124	0.082
(Fo−Fc)max[el/A^{-3}]	0.19/−0.20	0.22/−0.24
S (goof)	1.013	1.054

$w = 1/[\sigma^2(Fo^2) + (A * P)^2 + B * P]$ where $P = [\mathrm{Max}(F^2) + 2F^2]/3$ and A and B are refined parameters listed in Table I. Computing was performed with SHELXL93.[4] Listings of observed and anisotropic thermal parameters are available from the authors on request. Final atomic coordinates and equivalent isotropic displacements are presented in Tables II and III while Tables IV and V contain the interatomic distances and angles for compounds (I) and (II), respectively. It should be noted that the symmetry codes used in Table Va and Figure 5 are different from those used in Table Vb and shown in Figure 6.

DISCUSSION

The packing diagram of compound (I), displayed in Figure 1, reveals molecular layers composed of 2,5-pzdc molecules held together by hydrogen

TABLE II Fractional atomic coordinates and equivalent isotropic displacement (Å) for the pyrazine-2,5-dicarboxylic acid dihydrate structure. $Ueq = (U_{11}+U_{22}+U_{33})/3$

Atom	*x*	*y*	*z*	*Ueq*
O1	0.519(1)	0.022(1)	0.375(1)	0.048(1)
O2	−0.086(1)	1.807(1)	0.997(1)	0.050(1)
O3	−0.032(1)	1.406(1)	0.824(1)	0.050(1)
O4	0.463(1)	0.428(1)	0.544(1)	0.051(1)
O5	0.052(1)	0.294(1)	0.289(1)	0.045(1)
O6	0.378(1)	1.536(1)	1.082(1)	0.043(1)
C1	0.021(1)	0.759(1)	0.493(1)	0.036(1)
C2	0.428(1)	1.084(1)	0.880(1)	0.030(1)
C3	0.233(1)	0.700(1)	0.583(1)	0.030(1)
C4	0.242(1)	0.460(1)	0.459(1)	0.033(1)
C5	0.204(1)	1.137(1)	0.793(1)	0.029(1)
C6	0.195(1)	1.389(1)	0.916(1)	0.029(1)
N1	−0.001(1)	0.977(1)	0.600(1)	0.034(1)
N2	0.433(1)	0.862(1)	0.774(1)	0.032(1)
H1	−0.19(1)	0.62(1)	0.36(1)	0.02(1)
H2	0.53(1)	1.18(1)	1.03(1)	0.02(1)
H3	−0.01(1)	1.62(1)	0.91(1)	0.05(1)
H4	0.47(1)	0.30(1)	0.45(1)	0.03(1)
H11	0.67(1)	0.03(1)	0.47(1)	0.02(1)
H12	0.41(3)	−0.11(3)	0.24(3)	0.10(1)
H21	−0.04(3)	1.96(3)	1.10(3)	0.09(1)
H22	−0.20(1)	1.80(1)	0.99(1)	0.05(1)

TABLE III Fractional atomic coordinates and equivalent isotropic displacement (Å) for $[Mg(H_2O)_6]$ (2,5-pzdc). $Ueq = (U_{11}+U_{22}+U_{33})/3$

Atom	*x*	*y*	*z*	*Ueq*
Mg	0.0	0.0	0.5	0.0209(2)
01	−0.0179(1)	−0.2790(2)	0.5575(1)	0.0293(3)
02	0.0466(2)	0.0926(2)	0.6748(1)	0.0298(3)
03	−0.2624(1)	0.0250(2)	0.4935(1)	0.0313(3)
04	−0.1952(1)	−0.0311(2)	0.7995(1)	0.0287(3)
05	−0.4493(2)	0.0057(2)	0.6875(1)	0.0424(4)
N1	−0.3284(2)	−0.0329(2)	1.0036(1)	0.0258(3)
C1	−0.6026(2)	0.0244(3)	0.8960(1)	0.0273(4)
C2	−0.4317(2)	−0.0078(2)	0.8994(1)	0.0210(3)
C3	−0.3538(2)	−0.0120(2)	0.7848(1)	0.0233(3)
H1	−0.681(3)	0.042(4)	0.820(2)	0.037(6)
H11	0.056(3)	−0.358(4)	0.585(2)	0.043(6)
H12	−0.101(4)	−0.349(4)	0.535(2)	0.060(8)
H21	0.075(3)	0.205(4)	0.690(2)	0.051(7)
H22	−0.030(4)	0.064(4)	0.713(2)	0.062(9)
H31	−0.346(4)	0.013(4)	0.430(2)	0.046(7)
H32	−0.316(4)	0.022(4)	0.553(2)	0.052(8)

bonds between carboxylate oxygens and water molecules with $d_{O\cdots H-O}$ in the range from 2.51 Å to 3.07 Å (see Table IV). The 2,5-pzdc and water molecules constitute planes with maximum out-of-plane shifts of 0.02 Å. The carboxylic groups C4, O4, O4 and C6, O3, O6 make dihedral angles

TABLE IV Selected interatomic distances (in Å) and angles (in deg.) for pyrazine-2,5-dicarboxylic acid dihydrate

(a) Covalent bonds:			
C1–N1	1.35(1)	C1–N1–C5	114.3(7)
N1–C5	1.34(1)	N1–C5–C2	122.9(7)
C5–C2	1.41(1)	C5–C2–N2	119.1(8)
C2–N2	1.33(1)	C2–N2–C3	118.6(7)
N2–C3	1.32(1)	N2–C3–C1	121.9(7)
C3–C1	1.38(1)	C3–C1–N1	122.1(8)
C4–C3	1.48(1)	O4–C4–O5	121.9(8)
–O4	1.31(1)		
–O5	1.25(1)		
C6–C5	1.52(1)	O3–C6–O6	128.8(8)
–O3	1.29(1)		
–O6	1.18(1)		
O1–H11	0.91(4)	H11–O1–H12	126(9)
–H12	0.90(16)		
O2–H21	0.88(15)	H21–O2–H22	89(10)
–H22	0.60(8)		
(b) Hydrogen bonds:			
O4·········O1	2.54(1)	O4–H4·········O1	152(9)
H4······O1	1.81(9)		
O3a·········O2a	2.51(1)	O3a–H3a·········O2a	155(9)
H3a···O2a	1.25(9)		
O1·········O3b	3.07(1)	O1–H11·········O3b	124(9)
H11···O3b	2.46(9)		
O1·········O6a	2.80(1)	O1–H12·········O6a	135(10)
H12···O6a	2.08(11)		
O2a·········O5	2.80(1)	O2a–H21a·········O5	171(10)
H21a···O5	1.93(11)		
O1·············N1b	2.85(1)	O1–H11·········N1b	163(8)
H11···N1b	1.97(9)		
C1b·············O6a	3.51(1)	C1b–H1b·········O6a	145(8)
H1b······O6a	2.47(9)		

a: $x, y-2, z-1$.
b: $x+1, y-1, z$.

with the plane of the pyrazine ring amounting to 5.9° and 4.3° respectively (Figure 2). The interatomic distances and angles listed in Table IV are in fair agreement with those reported for other pyrazine carboxylic acids.[5,6] The interplanar spacing observed in compound (I) is 3.2 Å, so that much weaker van der Waals interactions may be assumed to be operating between the layers.

Molecular layers held by hydrogen bonds were found to be the characteristic feature of the structures of pyrazine-2-carboxylic[5] and pyrazine-2,3-dicarboxylic acids,[6] however, the structure of the latter displays a different pattern from that of 2,5-pzdc since the planes of the carboxylate groups are not coplanar with the pyrazine rings.

The 2,5-pzdc molecules in compound II have their centers at the symmetry centers. A simpified packing diagram (Figure 4) indicates that the

TABLE V Selected interatomic distances (in Å) and angles (in deg.) for $Mg(H_2O)_6$(2,5-pzdc)

(*a*) *Covalent bonds:*			
Mg-O1	2.034(1)	O1-Mg-O2	90.25(6)
Mg-O2	2.047(1)	O2-Mg-O3	91.74(6)
Mg-O3	2.100(1)	O3-Mg-O1	87.98(6)
C1-C2	1.382(2)	N1f-C1-C2	121.9(1)
C2-N1	1.333(1)	C1-C2-N1	120.9(1)
N1-C1f	1.340(2)	C2-N1-C1f	117.1(1)
C3-C2	1.526(2)	O4-C3-O5	126.1(1)
C3-O4	1.261(2)		
C3-O5	1.235(2)		
C1-H1	0.98(2)		
O1-H11	0.83(3)	H11-O1-H12	103(2)
-H12	0.83(3)		
O2-H21	0.82(3)	H21-O2-H22	108(3)
-H22	0.83(3)		
O3-H31	0.90(3)	H31-O3-H32	103(3)
-H32	0.86(3)		
f: $-x-1$, $-y$, $-z+2$			
(*b*) *Hydrogen bonds:*			
O3d··················.O5c	2.828(2)	O3d-H31d······.O5c	171(5)
H31d.O5c	1.94(3)		
O1b··················.O4c	2.757(2)	O1b-H11b······.O4c	161(5)
H11b.O4c	1.96(3)		
O2a··················.O4c	2.837(2)	O2a-H21a·········O4c	164(5)
H21a.O4c	2.04(3)		
O2c··················.O4c	2.710(2)	O2c-H22c·········O4c	176(5)
H22c.O4c	1.89(3)		
O3c··················.O5c	2.851(2)	O3c-H32c·········O5c	177(5)
H32c.O5c	1.99(3)		
O1··················.N1f	2.779(2)	O1-H12·········.N1f	166(5)
H12······.N1f	1.97(3)		
C1e··················O2	3.468(2)	C1e-H1e·········.O2	143(5)
H1e······.O2	2.52(3)		

a: $x, y, z-1$.
b: $x, y+1, z-1$.
c: $-x, y+1/2, 1/2-z$.
d: $x+1, 1/2-y, z-1/2$.
e: $x+1, y, z$.
f: $x-1, -y-1/2, z-1/2$.

2,5-pzdc molecules are aligned in layers normal to the *b* axis and illustrates the mutual alignment of the $Mg(H_2O)_6$ octaehedra and the planes of acid molecules.

The coordination of the magnesium ion is octahedral; six water molecules are located at the apices of a fairly regular octahedron with mean $d_{\mathrm{Mg-O}} = 2.061$ Å; typical for Mg-O bonds. The three planes passing through the Mg atom and the oxygens are almost perpendicular to each other with dihedral angles of 88.24°, 87.99° and 88.47° (Figure 5). Four acid molecules and the Mg ion make a plane with maximum shift from the mean plane amounting to 0.27(1) Å. The pyrazine rings are planar with maximum

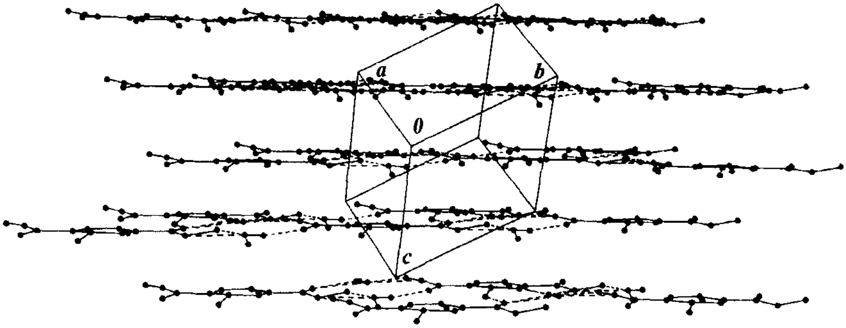

FIGURE 1 Packing diagram of the pyrazine-2,5-dicarboxylic acid dihydrate structure.

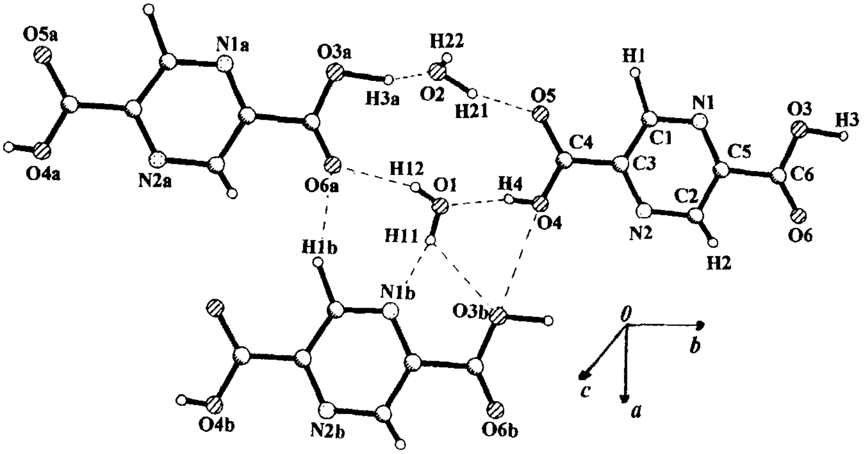

FIGURE 2 A fragment of the molecular plane in the structure of pyrazine-2,5-dicarboxylic acid dihydrate. The numbering of atoms refers to Tables II and IV. *a*: (x, $y-2$, $z-1$); *b*: ($x+1$, $y-1$, z).

out-of-plane shift of 0.01(1) Å. The plane of the carboxylic group is inclined to the plane of the pyrazine ring by 3.7(1)°. On the other hand, the plane formed by a Mg ion and four oxygens belonging to the octahedron (Mg, O2, O3 – see Figure 4) makes a dihedral angle of 18.8(1)° with the plane formed by a Mg ion and 4 acid molecules. The bond lengths and angles within the pyrazine ring and the carboxylate groups agree reasonably well with those found in the structure of compound (I).

The $Mg(H_2O)_6$ octahedra and the 2,5-pzdc molecules interact *via* a system of hydrogen bonds. One of the carboxylic oxygens – O4c (Figure 6) is linked by strong hydrogen bonds to 3 water molecules (O1b, O2a, O2c) belonging to the same $Mg(H_2O)_6$ octahedron with bond lengths of 2.757(2),

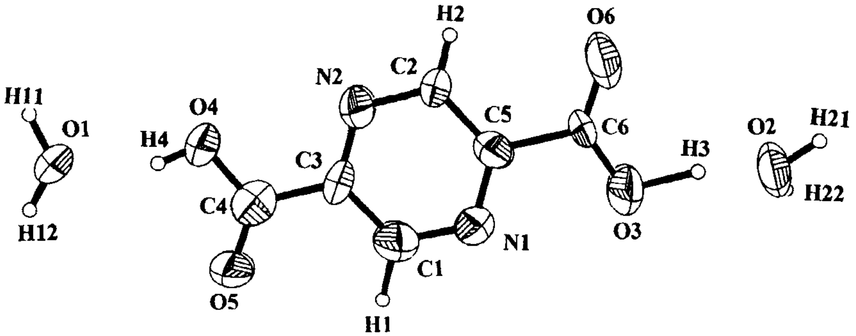

FIGURE 3 The pyrazine-2,5-dicarboxylic acid dihydrate molecule. ORTEP picture with thermal ellipsoids.

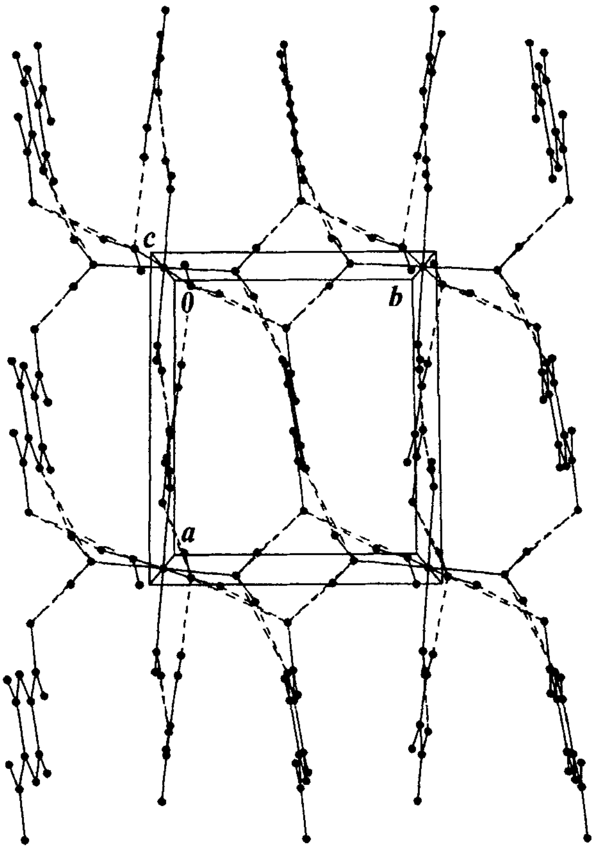

FIGURE 4 Packing diagram of the [Mg(H_2O)$_6$] (2,5-pzdc) structure.

2.837(2) and 2.710(2) Å, respectively (Table Vb). The second oxygen of this group O5c receives two hydrogen bonds from water molecules O3d and O3c with O5· · ·O3 distances of 2.828(2) Å and 2.851(2) Å, respectively.

Water molecules 1 and 3 (O1 and O3) have an almost planar trigonal environment. The deviation of Mg from the planes of water molecules 1 and 3 are 11° and 9°, respectively. Water 1 donates one hydrogen bond to the O4 atom and one to the N1 atom, while water 3 donates one to O5 and one to another O5 atom. Water 2 (O2), by contrast, has a complete tetrahedral environment. It receives a coordinative bond from Mg (angle of 40° to the water plane) and a very weak hydrogen bond (O2· · ·H1e–C1e) of 3.468(2) Å (Table V); two hydrogen bonds are donated to the two O4 atoms. $Mg(H_2O)_6$ octahedra have been found in the structure of the magnesium complex with nicotinic acid: $Mg(H_2O)_6$ (nicotinate)$_2 \cdot 4H_2O$[7] as well as in the structure of the $[Mg(H_2O)_6][Cu(2,3,5,6\text{-pztc})(H_2O)_2] \cdot 2H_2O$ complex,[8] in which the $[Mg(H_2O)_6]$ ions are situated in the space between the

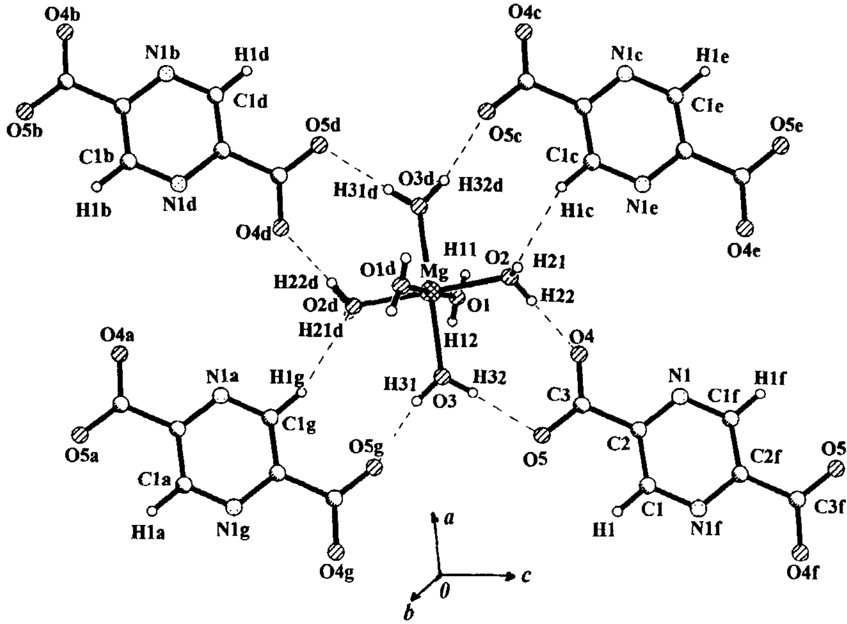

FIGURE 5 The environment of a $Mg(H_2O)_6$ octahedron in the structure of $[Mg(H_2O)_6]$ (2,5-pzdc) viewed along the *b* axis. The numbering of atoms refers to Tables III and Va. Dashed lines indicate the hydrogen bonds. *a*: $(x, y, z-1)$; *b*: $(x+1, y, z-1)$; *c*: $(x+1, y, z)$; *d*: $(-x, -y, -z+1)$; *e*: $(-x, -y, -z+2)$; *f*: $(-x-1, -y, -z+2)$; *g*: $(-x-1, -y, -z+1)$.

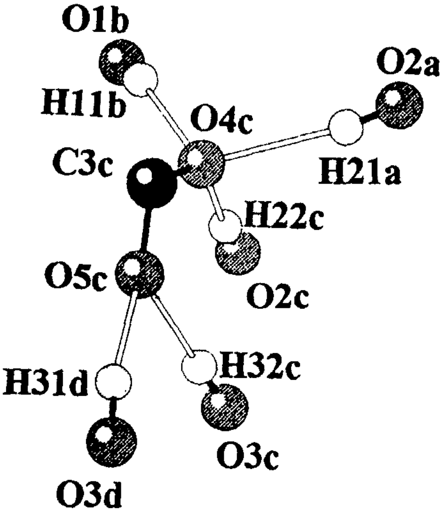

FIGURE 6 MOVIEMOL[9] picture of the hydrogen bond network in $[Mg(H_2O)_6]$ (2,5-pzdc). O4 and O5 carboxylic oxygens receives three and two hydrogen bonds, respectively. The numbering of atoms refers to Table Vb. *a*: $(x, y, z-1)$; *b*: $(x, y+1, z-1)$; *c*: $(-x, y+1/2, 1/2-z)$; *d*: $(x+1, 1/2-y, z-1/2)$.

$[Cu(2,3,5,6\text{-pztc})(H_2O)_2]$ molecular ribbons (2,3,5,6-pztc = pyrazine-2,3,5,6-tetracarboxylic acid). The latter are hydrogen bonded using the "free" carboxylic oxygens and the Mg coordinated water molecules.

The structure of compound (II) shows an entirely different pattern from that observed in the crystals of the magnesium complex with the pyrazine-2,3-dicarboxylic acid.[1] In the latter, molecular chains composed of Mg ions bridged by the 2,3-pzdc molecules have been discovered. Each Mg atom is octahedrally coordinated by a (N, O) moiety, an oxygen donated by a monodentate carboxylic group and three water molecules with typical Mg–N and Mg–O bond distances. This difference in coordination pattern may be due to the fact that the 2,5-pzdc molecule in the structure of compound (II) is centrosymmetric.

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