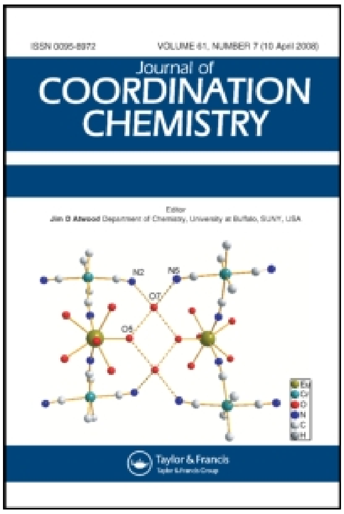

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The Crystal Structures of Pyrazine-2,6-Dicarboxylic Acid DihydRAte and Hexaaquamagnesium(II) Pyrazine-2,6-Dicarboxylate

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THE CRYSTAL STRUCTURES OF PYRAZINE-2,6-DICARBOXYLIC ACID DIHYDRATE AND HEXAAQUAMAGNESIUM(II) PYRAZINE-2,6-DICARBOXYLATE

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The crystals of the pyrazine-2,6-dicarboxylic acid dihydrate $[C_4H_2N_2(COOH)_2]\cdot 2H_2O$ or H_2(2,6-PZDC)] crystallize in the monoclinic system, space group C2/m. Their structure is composed of planar layers in which the acid and the water molecules interact via a network of hydrogen bonds. The layers are also hydrogen bonded.

Hexaaquamagnesium(II) pyrazine-2,6-dicarboxylate $[Mg(H_2O)_6]^{2+}[C_4H_2N_2(COO)_2]^{2-}$ crystallizes in the monoclinic system, space group $P2_1/n$. The magnesium(II) cation is surrounded by six water molecules located at the apices of an almost regular octahedron with the mean Mg–O bond distance of 2.068 Å. The 2,6-PZDC anions are planar and are acceptors in a network of hydrogen bonds donated by the coordinated water molecules.

Keywords: Pyrazine-2,6-dicarboxylic acid; Magnesium complex; X-ray crystal structure analysis.

INTRODUCTION

The presence of two carboxylic groups and two heteroring nitrogen atoms make pyrazine dicarboxylic acids very effective chelating agents. Therefore, metal complexes with the pyrazine dicarboxylate ligands show a variety of molecular patterns ranging from an ionic structure of magnesium pyrazine-2,5-dicarboxylate hexahydrate $Mg(H_2O)_6^{2+}(2,5\text{-PZDC})^{2-}$ [1], through molecular ribbons observed in the crystals of magnesium complex with pyrazine-2,3-dicarboxylate ligand [2] and two dimensional molecular layers detected in the calcium complex with the same ligand [3], to the three dimensional patterns reported in the strontium complexes with pyrazine-2,3-dicarboxylate [4] and pyrazine-2,5-dicarboxylate ligands [5]. In all of these complexes, except $Mg(H_2O)_6^{2+}(2,5\text{-PZDC})^{2-}$ [1], the oxygen atoms of one carboxylic group and the nearest heteroring nitrogen atom form a bonding moiety which chelates the metal ion, with the oxygen atom belonging to the other carboxylic group usually bridging either in

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monodentate or bidentate mode. Continuing our studies on the crystal chemistry of divalent metal compounds with pyrazine carboxylate ligands, we examined complexes with pyrazine-2,6-dicarboxylate, in which both carboxylic groups are close to only one heteroring nitrogen atom. We report in this paper the results of the X-ray diffraction study on the crystal and molecular structures of pyrazine-2,6-dicarboxylic acid dihydrate and its magnesium complex.

EXPERIMENTAL

Pyrazine-2,6-dicarboxylic acid dihydrate was recrystallized from water. The synthesis of the magnesium complex was carried out by dissolving 1 mmol of H_2(2,6-PZDC) · H_2O and 1 mmol of magnesium nitrate in 50 mL of hot water. After boiling for one hour the solution was left to crystallize. Colorless, plate-like single crystals were found after slow evaporation to dryness at room temperature. The dimensions of the crystals chosen for collection of X-ray diffraction data are given in Table I.

X-ray reflections were measured at room temperature using a KUMA KM4 (MoK_α radiation) four circle diffractometer operating in ω-2θ mode. Two standard reflections

TABLE I Crystal data and structure refinement details for H_2(2,6-PZDC) · $2H_2O$ and $Mg(H_2O)_6$ (2,6-PZDC)

Empirical formula	$C_6H_8N_2O_6$	$C_{12}H_{28}N_4O_{20}$ Mg_2
Formula weight	208.14	597.0
Temperature	293K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	monoclinic
Space group	C2/m	$P2_1/n$
Unit cell dimensions	$a = 12.060(2)$ Å	14.300(3) Å
	$b = 11.440(2)$ Å	11.600(2) Å
	c = 7.030(1) Å	15.110(3) Å
	$\beta = 117.429(3)°$	109.64(3)°
	V = 861.95. Å^3	2360.63 Å^3
Z	4	4
Calculated density	1.573 gcm 3	1.680 gcm 3
μ (Mo$K\alpha$)	0.14 mm^{-1}	0.21 mm^{-1}
F(000)	424.0	1248.0
Crystal size	0.2 × 0.2 × 0.4 mm^3	0.3 × 0.3 × 0.4 mm^3
Max 2θ for data collection	59.99°	52.09°
Index range	$0 \leq h \leq 15$	$-17 \leq h \leq 0$
	$0 \leq k \leq 15$	$-14 \leq k \leq 0$
	$-9 \leq l \leq 5$	$-15 \leq l \leq 17$
Number of measured reflections	935	3191
Number of reflections with $Fo > 4\sigma(F_o)$	655	2503
R_{int}	0.012	0.017
Method of structure solution	direct method	
Method of structure refinement	full-matrix least squares on F^2	
Number of parameters refined	88	455
Goodness-of-fit on F^2	1.090	1.080
Final Rl [$F_o > 4\sigma(F_o)$]	0.0324	0.0336
Final wR2 index	0.0934	0.0992
Absorption correction	none	ψ-scan
Minimum and maximum transmission factors	none	0.897, 0.918
Largest diff peak and hole	0.27 e/Å^3 and −0.17 e/ Å^3	0.31 e/Å^3 and −0.22 eÅ^3
Weight parameters (A,B)	0.0634, 0.00	0.0554, 1.51
Mean shift/esd	0.022	0.039

were monitored every 200 reflections. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections ($20° < 20 < 30°$). Reflections were processed using profile analysis and corrected for Lorentz factor and polarization effects. No absorption correction was applied in the case of H_2(2,6-PZDC)$\cdot 2H_2O$, however, an empirical absorption correction based on ψ-scan was applied for Mg$(H_2O)_6$(2,6-PZDC). Nonhydrogen atoms were located by direct methods using the SHELXLS program [6] and hydrogen atoms were then found by successive Fourier syntheses. Final refinement on F^2 by 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: $w=1/[\sigma^2+(A \times P)^2 + B \times P]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. A, B are the parameters listed in Table I. Calculations were carried out using the SHELXL97 program [7]. Selected bond lengths and angles are shown in Table II. Lists of the observed and calculated X-ray intensities, atomic coordinates and temperature factors are available from the authors on request.

DISCUSSION

Figure 1 shows two molecules of the title compound I with the atom numbering. Acid and water molecules in the crystals of H_2(2,6-PZDC)$\cdot 2H_2O$ interact *via* a network of hydrogen bonds. Both hydroxy groups of each acid molecule donate their hydrogen atoms to bonding the water molecule O4 forming molecular chains propagating along the *a* axis in the crystal. However, the water molecule O4 acts also as a donor in the hydrogen bond O4-H42$\cdots$N2 [2.752(3) Å] which links it with the heteroring nitrogen atom N2 belonging to a pyrazine ring in the adjacent chain, thus giving rise to molecular layers which are normal to the *c* axis. The acid molecules are almost planar: maximum shifts from the mean plane are −0.015(l) and 0.012(1) Å. As in the structure of pyrazine-2,5-dicarboxylic acid dihydrate [1], both carboxylic groups are coplanar with the pyrazine ring. The water molecule O3 is situated at 0.106(4) Å and the water molecule O4 at 0.941(4) Å above the plane of the layer. The water molecule O3 is hydrogen bonded to both carboxylate oxygen atoms of each acid molecule with a bond length of 2.968(2) Å. However, this water molecule also interacts with the O4 water molecule in the adjacent layer *via* a hydrogen bond O4–H41$\cdots$03^{III} [2.677(3) Å] constituting the interlayer link. The bond distances and angles in the molecule of the title compound are in fair agreement with those observed in pyrazine-2,3-dicarboxylic acid dihydrate [8] and pyrazine-2,5-dicarboxylic acid dihydrate [1] crystals.

The structure of hexaquamagnesium(II) pyrazine-2,6-dicarboxylate contains cations composed of Mg ions and six water molecules. The cations (anions) are located in two symmetry nonequivalent sites. Each Mg ion is surrounded by six water oxygen atoms situated at the apices of an almost regular octahedron. The observed Mg–O bond distances and bond angles listed in Table II are typical for this cation [1,9,10]. The pyrazine rings of both symmetry nonequivalent anions are planar, since maximum shifts from the respective average planes are: +0.017(2) Å (the C15 atom), −0.015(2) Å (the C13 atom) +0.035(2) Å (the N21 atom), and −0.044(2) Å (the C28 atom). On the other hand, the carboxylate oxygen atoms deviate from these planes from +0.067(4) Å (the O4 atom) to −0.023(3) Å (the O3 atom) and from +0.174(3) Å (the atom O8) to −0.310(4) Å (the atom O7). The interatomic distances and bond angles

TABLE II Selected interatomic distances (in Å) and bond angles (in degrees)

A) Pyrazine-2, 6-dicarboxylic acid dihydrate				
N1–C2	1.331(2)		$\mathrm{C2}^{I}$–N1–C2	116.7(2)
C2–C3	1.395(2)		N1–C2–C3	121.2(1)
C3–N2	1.332(2)		C2–C3–N2	121.2(1)
			C3–N2–C3	117.2(2)
C2–C7	1.505(2)			
C7–O1	1.216(2)		O1–C7–O2	125.4(1)
C7–O2	1.305(2)			
O2–H2	0.75(3)			
O3–H31	0.79(2)		H31–O3–H31	107(3)
O4–H41	0.88(4)		H41–O4–H42	104(3)
O4–H42	0.77(4)			
Hydrogen bonds:				
D–H···A	D···A	H···A	D–H–A	
O2–H2···$\mathrm{O4}^{III}$	2.624(2)	1.88(3)	172(3)	
O3–H31···O1	2.968(2)	2.18(2)	178(2)	
O3–H31···N1	3.040(3)	2.65(2)	112(2)	
O4–H42···N2	2.752(3)	2.01(4)	159(3)	
O4–H41···$\mathrm{O3}^{II}$	2.677(3)	1.80(4)	172(3)	
Symmetry code: $(^{I})$ $x, -y, z$; $(^{II})$ $-x, -y, -z+2$; $(^{III})$ $x+1/2, y+1/2, z$.				
B) Hexaqua magnesium(II) pyrazine-2,6-dicarboxylate				
Mgl–O11	2.038(2)		O11–Mgl–O12	175.6(1)
Mgl–O12	2.086(3)		O11–Mgl–O13	89.6(1)
Mgl–O13	2.084(3)		O13–Mg1–O14	87.2(1)
Mgl–O14	2.055(3)		O14–Mgl–O16	173.2(1)
Mgl–O15	2.091(2)		O15–Mgl–O13	176.1(1)
Mgl–O16	2.062(3)		O16–Mgl–O13	90.0(1)
Mg2–O21	2.100(3)		O21–Mg2–O22	172.1(1)
Mg2–O22	2.057(3)		O21–Mg2–O23	87.1(1)
Mg2–O23	2.104(3)		O23–Mg2–O24	88.3(1)
Mg2–O24	2.043(3)		O24–Mg2–O26	176.7(1)
Mg2–O25	2.082(3)		O25–Mg2–O23	176.9(1)
Mg2–O26	2.026(3)		O26–Mg2–O23	94.5(1)
N11–C12	1.332(4)		C16–N11–C12	117.4(3)
C12–C13	1.382(4)		N11–C12–C13	121.3(3)
C13–N12	1.331(4)		C12–C13–N12	122.2(3)
N12–C15	1.334(4)		C13-N12-C15	116.2(3)
C15–C16	1.387(4)		N12–C15–C16	122.2(3)
C16-N11	1.336(4)		C15–C16–N11	120.8(3)
C12–C17	1.513(4)			
C17–O1	1.234(4)		O1–C17–O2	126.0(3)
C17–O2	1.257(4)			
C16–C18	1.507(4)			
C18–O3	1.260(4)		O3–C18–O4	125.4(3)
C18–O4	1.250(4)			
N21–C22	1.347(4)		C26–N21–C22	117.9(2)
C22–C23	1.385(4)		N21–C22–C23	120.5(3)
C23–N22	1.333(5)		C22–C23–N22	122.0(3)
N22–C25	1.324(4)		C23–N22–C25	116.5(3)
C25–C26	1.391(4)		N22–C25–C26	122.6(3)
C26–N21	1.323(4)		C25–C26–N21	120.4(3)
C22–C27	1.516(4)			
C27–O5	1.250(4)		O5–C27–O6	125.6(3)
C27–O6	1.243(4)			
C26–C28	1.517(4)			

(*continued*)

TABLE II Continued

C28–O7	1.241(3)	O7–C28–O8	124.8(3)
C28–O8	1.270(3)		
O11–H111	0.95(5)	H111-O11–H112	103(4)
O11–H112	0.75(4)		
O12–H121	0.80(4)	H121–O12–H122	115(4)
O12–H122	0.92(5)		
O13–H131	0.76(6)	H131–O13–H132	106(6)
O13–H132	0.92(7)		
O14–H141	0.86(4)	H141–O14–H142	110(4)
O14–H142	0.82(5)		
O15–H151	0.92(5)	H151–O15–H152	110(4)
O15–H152	0.91(5)		
O16–H161	0.88(5)	H161–O16–H162	102(4)
O16–H162	0.91(5)		
O21–H211	0.82(4)	H211–O21–H212	109(5)
O21–H212	0.80(6)		
O22–H221	0.91(5)	H221–O22–H212	119(4)
O22–H222	0.85(5)		
O23–H231	0.88(4)	H231–O23–H232	104(4)
O23–H232	0.89(4)		
O24–H241	0.89(5)	H241–O24–H242	107(4)
O24–H242	0.94(5)		
O25–H251	0.88(5)	H251–O25–H252	114(5)
O25–H252	0.81(5)		
O26–H261	0.98(5)	H261–O26–H262	110(4)
O26–H262	0.74(4)		
Hydrogen bonds:			
D–H···A	D···A	H···A	D–H–A
O11–H11 ···O1^{XI}	2.812(4)	2.06(4)	173(4)
O11–H111···N11^{XI}	2.921(4)	2.51(4)	116(4)
O11–H112···O4^{XI}	2.823(4)	1.90(4)	166(4)
O12–H121···O3^{I}	2.726(3)	1.93(4)	173(4)
O12–H122···O2	2.675(3)	1.76(4)	170(4)
O13–H131···O4^{I}	3.047(4)	2.43(4)	139(4)
O13–H131 ···O15^{XI}	3.079(4)	2.58(4)	125(4)
O13–H132···O2^{VI}	2.747(4)	1.89(4)	155(4)
O14–H141···N12^{VII}	2.782(4)	1.94(4)	162(4)
O14–H142···O4^{I}	2.821(4)	2.06(4)	155(4)
O15–H151···O8^{XII}	2.939(4)	2.05(4)	162(4)
O15–H152 ···O1	2.603(4)	1.70(4)	172(4)
O16–H161 ···O3^{V}	2.828(4)	1.99(4)	160(4)
O16–H162···O5	2.986(4)	2.30(4)	132(3)
O21–H211···O12^{II}	3.075(4)	2.27(4)	167(4)
O21–H212···O8^{X}	2.798(4)	2.00(4)	171(4)
O22–H221···O7^{IX}	2.791(4)	1.92(4)	159(4)
O22–H222···N22	2.783(4)	1.94(4)	171(4)
O23–H231···O6^{VIII}	2.748(4)	1.87(4)	176(4)
O23–H232···O3^{III}	2.852(4)	1.98(4)	168(4)
O24–H241···O5^{IV}	2.861(4)	1.98(4)	171(4)
O24–H241···N21^{IV}	2.912(4)	2.48(4)	110(3)
O24–H242···O7^{IV}	2.800(3)	1.86(4)	174(4)
O25–H251···O5^{VII}	2.719(4)	1.86(4)	167(4)
O26–H261···O8^{IX}	2.803(3)	1.84(4)	167(4)
O26–H262···O6^{VII}	2.764(3)	2.03(4)	172(4)

Symmetry code:
(^{I}): $x, y-1, z$; (^{II}): $x, y, z-1$; (^{III}): $x, y-1, z-1$; (^{IV}): $-x+1, -y, -z+1$;
(^{V}): $-x+1, -y+1, -z+2$; (^{VI}): $-x+1, -y, -z+2$; (^{VII}): $x-112, -y+112, z-112$;
(^{VIII}): $-x+1/2, y-1/2, -z+1/2$; (^{IX}): $x-1/2, -y-1/2, z-1/2$; (^{X}): $-x+1/2, y+1/2, -z+1/2$;
(^{XI}): $-x+1/2, y-1/2, -z+3/2$; (^{XII}): $-x+1/2, y+1/2, -z+3/2$.

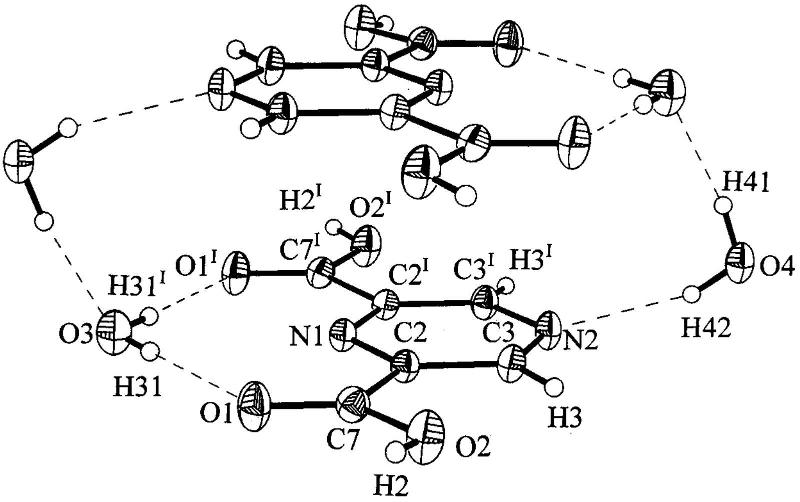

FIGURE 1 Two molecular units of pyrazine-2,6-dicarboxylic acid dihydrate belonging to adjacent layers with the atom numbering scheme. The nonhydrogen atoms are shown as 50% probability ellipsoids. Atoms with the index ^{I} are generated by symmetry operation x, $-y$, z. Dashed lines indicate hydrogen bonds.

determined for both anions do not differ from those observed in the parent acid (title compound 1).

The $[Mg(H_2O)_6]^{+2}$ cations and $(2,6\text{-PZDC})^{-2}$ anions interact using a network of hydrogen bonds with the lengths in the range from 2.70 to 3.01 Å, in which the coordinated water molecules act as donors, the acceptors being either the carboxylate oxygen atoms or the heteroring nitrogen atoms in the adjacent anions. These bonds are listed in detail in Table II. The cations and anions are packed in the crystal as layers, with the anions on two levels. Each layer contains atoms belonging to one of the two symmetry non-equivalent sites. Figure 2 shows a fragment of one of the layers consisting of two cations and two anions with the atom numbering scheme. Figure 3 shows a fragment of another layer with Mg1 cations. For clarity, the anions situated on only one level are displayed.

The structure of the title compound II confirms the strong preference of the Mg(II) ion to acquire octahedral coordination. For magnesium(II) complexes with carboxylate ligands containing azine rings, three modes of coordination may be distinguished; in all of them the coordination remains octahedral. Mg(II) coordinated by six water oxygen atoms and azine carboxylate anions interacting with coordinated water molecules *via* extended system of hydrogen bonds have been detected in crystals of hexaqua magnesium pyrazine-2,5-dicarboxylate [1], magnesium nicotinate [9] and the complex with composition $[Mg(H_2O)_6][Cu(2,3,5,6\text{-PZTC})(H_2O)_2]\cdot H_2O$,(2.3,5,6-PZTC = pyrazine-2,3,5,6-tetracarboxylate ligand) [10]. Monomeric molecules composed of Mg(II) ions coordinated by two ligand molecules *via* their N,O bonding moieties and two water oxygen atoms have been discovered in the structures of magnesium picolinate [11] and aminopyrazinate [12]. Mg ions coordinated by two oxygen atoms, each donated by a different carboxylate group of the ligand, the pyridine nitrogen atom and three water oxygen atoms forming a monomeric moiety were observed in the structure of magnesium dipicolinate [13]. On the other hand, molecular ribbons have been detected in the structure of the complex with pyrazine-2,3-dicarboxylate and water ligands [2].

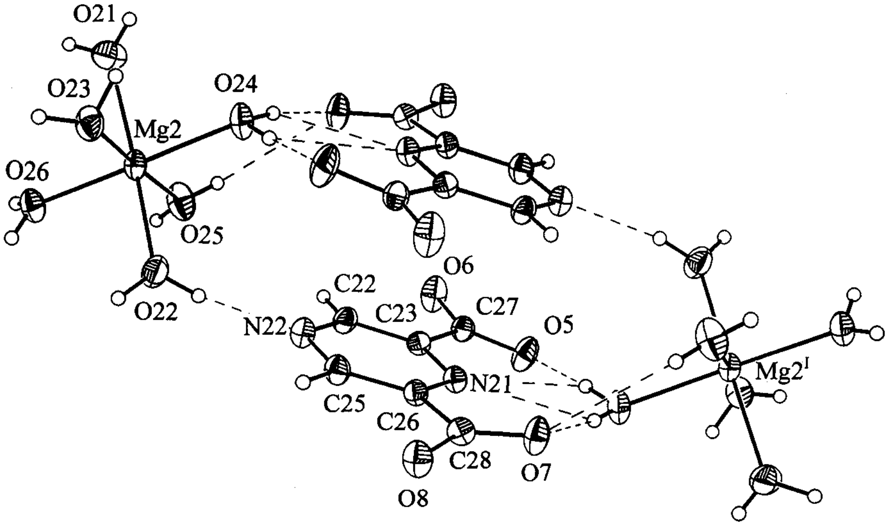

FIGURE 2 Two cation–anion assemblies in the structure of $Mg(H_2O)_6$ (2,6-PZDC) with atom numbering scheme. The anions are on two levels in the layer. The nonhydrogen atoms are shown as 50% probability ellipsoids. Dashed lines indicate hydrogen bonds.

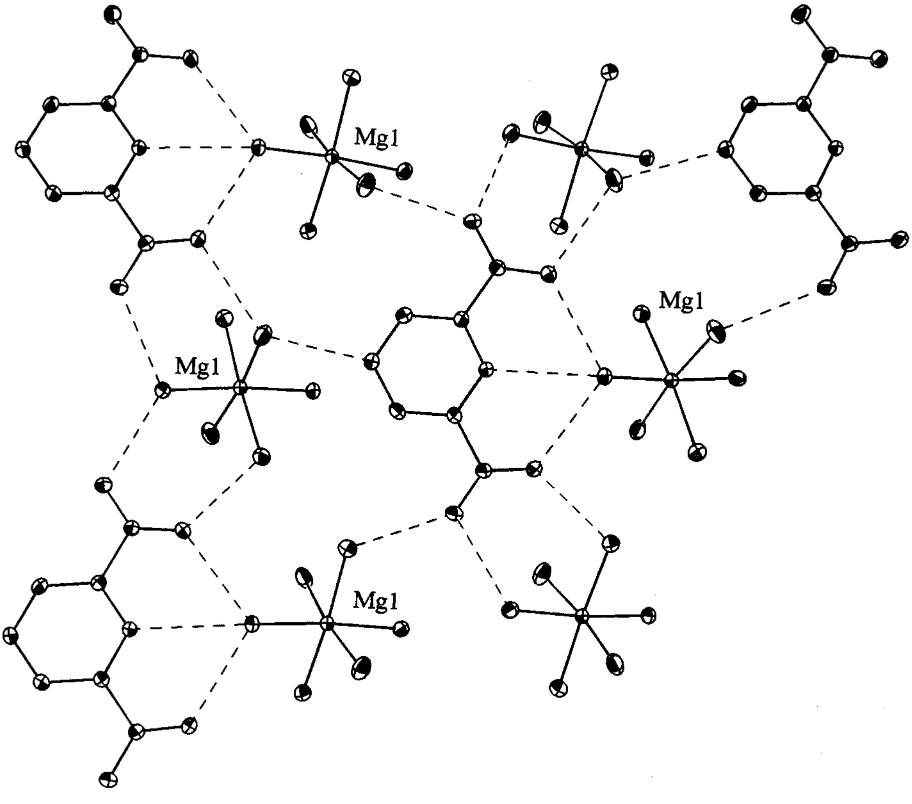

FIGURE 3 The alignment of cations and anions in a layer in the structure of $Mg(H_2O)_6$ (2,6-PZDC). For clarity, only anions situated on one level are shown.

In this structure, each ligand molecule bridges two adjacent Mg(II) ions using its N,O bonding moiety and a monodentate oxygen atom donated by the other carboxylate group. Three water molecules complete a fairly regular octahedral environment around each Mg ion.

The available structural data on Mg(II) complexes with azine carboxylate ligands indicate that octahedral coordination is strongly preferred. The occurrence of hexahydrate Mg ions in a number of compounds might suggest that the Mg(II) ion prefers to avoid the coordination by either N,O bonding or both oxygen atoms of a bidentate carboxylic group which would force considerable distortion of the octahedral coordination. However, the existence of monomeric molecules, and even a polymeric pattern in which the N,O bonding moieties are active in coordination but the octahedral environment is preserved, contradicts this suggestion.

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