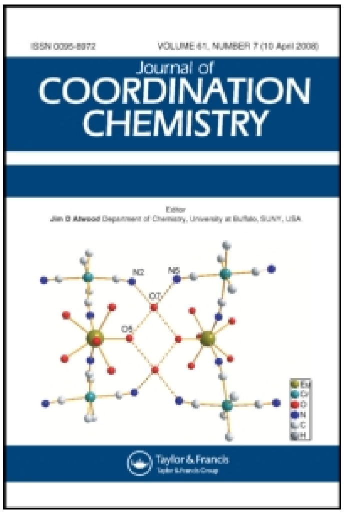

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THE CRYSTAL AND MOLECULAR STRUCTURE OF AN IONIC HYDRAZINIUM MAGNESIUM(II) COMPLEX WITH PYRIDAZINE-3,6-DICARBOXYLATE AND WATER LIGANDS

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The structure of hydrazinium magnesium(II) pyridazine-3,6-dicarboxylate comprises two univalent hydrogen hydrazine cations, a divalent di(aqua-*O*)bis(pyridazine-3,6-dicarboxylato-*N*,*O*) magnesium(II) anion and two solvate water molecules in the triclinic unit cell. The magnesium(II) ion is located on the center of symmetry. The coordination around the magnesium(II) ion is slightly distorted octahedral. The ligand molecules are coplanar. Their N,O bonding moieties coordinated to the metal ion form the equatorial plane of the distorted octahedron (Mg–O 2.062 Å, Mg–N 2.176 Å) with two water ligands in the *trans* axial sites (Mg–O 2.047 Å).

Keywords: Magnesium; X-ray structure; Pyridazine-3,6-dicarboxylate

INTRODUCTION

The structures of magnesium(II) complexes with azine and diazine dicarboxylate ligands that have been determined show octahedral coordination of the Mg(II) ion but different molecular patterns. Highly distorted octahedral coordination of the metal ion to three water oxygen atoms, one hetero ring nitrogen atom and two oxygen atoms donated by two monodentate carboxylic groups has been observed in the structure of the complex with pyridine-2,6-dicarboxylate (dipicolinate or 2,6-PDDC) and water ligands [1]. The crystals of this complex contain monomeric molecules of $Mg(2,6\text{-}PDDC)(H_2O)_3$. On the other hand, molecular chains composed of Mg(II) ions bridged by pyrazine-2,3-dicarboxylate (2,3-PZDC) ligands have been found in the structure of this complex. The 2,3-PZDC ligand donates one oxygen atom belonging to one of its carboxylate groups to the coordination of an Mg(II) ion on one side, while an oxygen from its second carboxylate group and the nearest hetero ring nitrogen atom (an N,O bonding moiety) are linked to an adjacent

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TABLE I Crystal data and structure refinement details for $(H_2N{\cdot}NH_3)^+{}_2[Mg(3,6\text{-}PRDC)_2(H_2O)_2]^{2-}{\cdot}2H_2O$

Empirical formula	$C_{12}H_{24}N_8O_{12}Mg$
Formula weight	496.70
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 6.930(1)$ Å $b = 9.011(2)$ Å $c = 9.018(2)$ Å $\alpha = 91.46(3)^\circ$ $\beta = 97.08(3)^\circ$ $\gamma = 112.37\ (3)^\circ$ $V = 515.18$ Å^3
Z	2
Calculated density	1.601 g cm^{-3}
μ (Mo Kα)	0.17 mm^{-1}
$F(000)$	260.0
Crystal size	0.2 × 0.2 × 0.3 mm
Max. 2θ for data collection	60.20°
Index range	$0 \le h \le 9,\ -12 \le k \le 11,\ -12 \le l \le 12$
No. of measured reflections	3003
No. of unique reflections with $F_o > 4\sigma(F_o)$	2162
R_{int}	0.0587
Method of structure solution	Direct method
Method of structure refinement	Full-matrix least-squares on F^2
No. of parameters refined	199
Goodness-of-fit on F^2	1.048
Final $R1$ $[F_o > 4\sigma(F_o)]$	0.0393
Final $wR2$ index	0.1242
Largest diff. peak and hole	0.65 and −0.22 e Å^{-3}
Weight parameters (A, B)	0.0857, 0.0345
Mean shift/esd	0.002

Mg(II) ion. Three water oxygen atoms complete a fairly regular environment for each metal ion [2]. The structures of Mg(II) compounds with pyrazine-2,5-dicarboxylate and pyrazine-2,6-dicarboxylate show ionic patterns consisting of hexaqua magnesium cations and the relevant pyrazine dicarboxylate anions [3,4].

EXPERIMENTAL

The magnesium complex with the pyrazidine-3,6-dicarboxylate ligand was obtained by reacting hot aqueous solutions of magnesium(II) acetate tetrahydrate and pyridazine-3,6-dicarboxylic acid dihydrate in a 1 : 1 molar ratio. After boiling for 2 h, the solution was left to crystallize at room temperature. However, after evaporation to dryness, crystalline material, unsuitable for collection of X-ray data, was found at the bottom of the crystallization pot. The material was therefore dissolved in cold water with the addition of a few drops of hydrazine. After evaporation to dryness, colorless, well-formed, single crystals could be selected for X-ray measurements.

X-ray reflections were measured at room temperature using a KUMA KM4 four circle diffractometer operating in $\omega - 2\theta$ mode. Two standard reflections were monitored every 200 reflections. Unit cell dimensions and standard deviations were obtained

TABLE II Atomic coordinates and equivalent isotropic displacements (Å^2) for $(H_2N{\cdot}NH_3)^+{}_2[Mg(3,6\text{-}PRDC)_2(H_2O)_2]^{2-}{\cdot}2H_2O$.

Atom	*x*	*y*	*z*	U_{eq}
Mg	0	0.5	0.5	0.0248(2)
C3	−0.0065(2)	0.3020(1)	0.9711(1)	0.0217(2)
C4	0.0322(2)	0.2489(1)	0.8984(1)	0.0265(2)
C5	0.1702(2)	0.3615(1)	1.0070(1)	0.0261(2).
C6	0.2568(2)	0.5207(1)	0.9711(1)	0.0217(2)
C7	0.1644(2)	0.8062(1)	0.3693(1)	0.0251(2)
C8	0.3944(2)	0.6569(1)	0.0880(1)	0.0242(2)
N1	0.2199(2)	0.5661(1)	0.8349(1)	0.0241(2)
N2	0.0896(2)	0.4549(1)	0.7291(1)	0.0233(2)
O1	0.1866(2)	0.7390(1)	0.4878(1)	0.0302(2)
O2	0.2594(2)	0.9483(1)	0.3469(1)	0.0383(2)
O3	0.4587(2)	0.7949(1)	1.0459(1)	0.0393(3)
O4	0.4284(2)	0.6183(1)	1.2172(1)	0.0361(2)
H4	−0.031(3)	0.142(2)	0.920(2)	0.038(5)
H5	0.203(3)	0.331(2)	1.097(2)	0.040(5)
O5	0.2137(2)	0.4248(2)	0.4191(1)	0.0402(3)
H51	0.287(4)	0.476(3)	0.360(3)	0.056(6)
H52	0.252(3)	0.360(3)	0.461(2)	0.053(6)
O11	0.2838(2)	0.1879(1)	0.5561(1)	0.0388(3)
H111	0.396(4)	0.242(3)	0.623(3)	0.054(6)
H112	0.328(4)	0.135(3)	0.497(3)	0.068(7)
N11	0.1209(2)	0.9062(2)	0.7720(2)	0.0410(3)
N12	0.3352(2)	0.9198(1)	0.7790(1)	0.0317(2)
H11	0.042(4)	0.805(4)	0.714(3)	0.085(8)
H12	0.107(3)	0.981(3)	0.722(3)	0.052(6)
H21	0.361(3)	0.853(2)	0.838(2)	0.034(4)
H22	0.416(3)	1.018(3)	0.823(2)	0.051(6)
H23	0.367(4)	0.905(3)	0.686(3)	0.056(6)

U_{eq} is defined as one-third of the trace of the orthogonal U_e tensor.

by least-squares fit to 25 reflections (15° < $2\theta < 30°$). Reflections were processed using profile analysis and corrected for Lorentz and polarization effects. Nonhydrogen atoms were located by direct methods using the SHELXLS program [5] and hydrogen atoms were then found by successive Fourier syntheses. Final refinement on F^2 by full-matrix least-squares methods using SHELXL97 [6] was carried out on positional parameters of all atoms, anisotropic vibrational parameters of all nonhydrogen atoms and isotropic temperature factors of hydrogen atoms. A weighting scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$. A and B are the parameters listed in Table I. Final atomic coordinates and equivalent isotropic displacements are listed in Table II. Selected bond lengths and angles are collected in Table III. The 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 234182.

DISCUSSION

The structure of the title compound is composed of $[Mg(3,6\text{-}PRDC)_2(H_2O)_2]^{2-}$ (3,6-PRDC = pyridazine-3,6-dicarboxylate) anions and $(H_3H{\cdot}NH_2)^+$ cations. In addition, there are two solvate water molecules per unit cell. The Mg(II) atom, situated in the

TABLE III Selected bond lengths (Å) and angles (°) in $(H_2N\cdot NH_3)^+{}_2[Mg(3,6\text{-}PRDC)_2(H_2O)_2]^{2-}\cdot 2H_2O$

Mg–O1	2.062(1)		O1–Mg–N1	76.54(5)
Mg–N2	2.176(1)		O1–Mg–O5	92.31(5)
Mg–O5	2.047(1)		N1–Mg–O5	92.77(5)
N1–N2	1.334(1)		C6–N1–N2	118.6(1)
N2–C3	1.333(2)		N1–N2–C3	121.2(1)
C3–C4	1.390(2)		N2–C3–C4	121.9(1)
C4–C5	1.372(2)		C3–C4–C5	117.2(1)
C5–C6	1.393(2)		C4–C5–C6	118.0(1)
C6–N1	1.330(2)		C5–C6–N1	122.9(1)
C3–C7	1.517(2)			
C7–O1	1.263(2)			
C7–O2	1.232(2)		O1–C7–O2	126.9(1)
C6–C8	1.524(2)			
C8–O3	1.239(2)		O3–C8–O4	126.5(1)
C8–O4	1.244(2)			
Hydrogen bonds				
D–H$\cdots$A	D–A	D–H	H$\cdots$A	D–H–A
N11–H11$\cdots$O5^{IV}	3.275(2)	1.00(3)	2.32(3)	160(2)
N11–H11$\cdots$O1	3.106(2)	1.00(3)	2.43(3)	124(2)
N11–H12$\cdots$O11^{II}	3.182(2)	0.84(2)	2.50(3)	147(2)
N12–H21$\cdots$O3	2.856(2)	0.87(2)	2.07(2)	150.1(2)
N12–H21$\cdots$N1	3.049(2)	0.87(2)	2.38(3)	134.4(2)
N12–H22$\cdots$O3^{VII}	2.756(2)	0.85(2)	1.95(2)	160.0(2)
N12–H23$\cdots$O1	2.906(2)	0.91(3)	2.21(3)	133(2)
N12–H23$\cdots$O2^{VI}	2.986(2)	0.91(3)	2.49(3)	115.3(2)
O5–H51$\cdots$O4^{I}	2.724(2)	0.82(2)	1.92(2)	171(3)
O5–H52$\cdots$O11	2.664(2)	0.79(2)	1.99(2)	167(2)
O11–H111$\cdots$O4^{V}	2.714(2)	0.89(3)	1.86(2)	160(2)
O11–H112$\cdots$O2^{III}	2.774(2)	0.78(3)	2.07(3)	150(3)

center of symmetry, coordinates two 3,6-PRDC ligands, each through the carboxylate oxygen atom and the nearest hetero ring nitrogen atom. The second oxygen atoms of these carboxylate groups remain coordinated. The other carboxylate group of 3,6-PRDC does not coordinate the Mg(II). The atoms forming the pyrazine ring and both carboxylate groups are almost coplanar as the maximum shifts from the least-squares plane range from + 0.107 Å (the N2 atom) to −0.110 Å (the O2 atom). The observed bond lengths and angles within the pyrazidinate ring compare well with those reported for the pyridazine-3,6-dicarboxylic acid dihydrate [7]. A careful analysis of the Fourier maps did not indicate the presence of hydrogen atoms bonded to the carboxylate oxygen atoms. On the contrary, an additional hydrogen atom attached to one hydrazine amino group was readily located. $(NH_3\cdot NH_2)^+$ cations were thus identified. As there are two hydrazine molecules in a unit cell, the charge balance is maintained. Figure 1 shows an anion, a cation and a solvation water molecule with the atom-labeling scheme, and Fig. 2 shows the packing diagram of the title compound.

The hydrazine cation is a donor in a network of rather weak hydrogen bonds with the donor–acceptor distances around 3 Å (see Table III). The only exception is the N12–H22$\cdots$O3^{VII} bond with a distance of 2.756(2) Å. On the other hand, the hydrogen bonds in which solvate and coordination water molecules act as donors are stronger, as indicated by the relevant bond distances, which range from 2.664(2) to 2.774(2) Å.

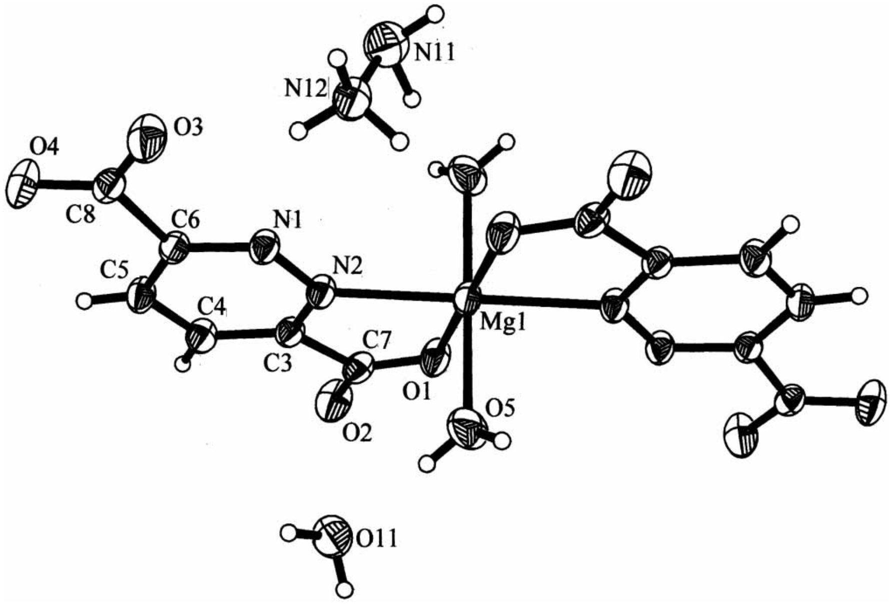

FIGURE 1 The view of a $(H_2N{\cdot}NH_3)^+$ cation, a $[Mg(3,6\text{-PRDC})_2(H_2O)_2]^{2-}$ anion and a solvation water molecule with the atom-numbering scheme. The nonhydrogen atoms are shown as 50% probability elipsoids.

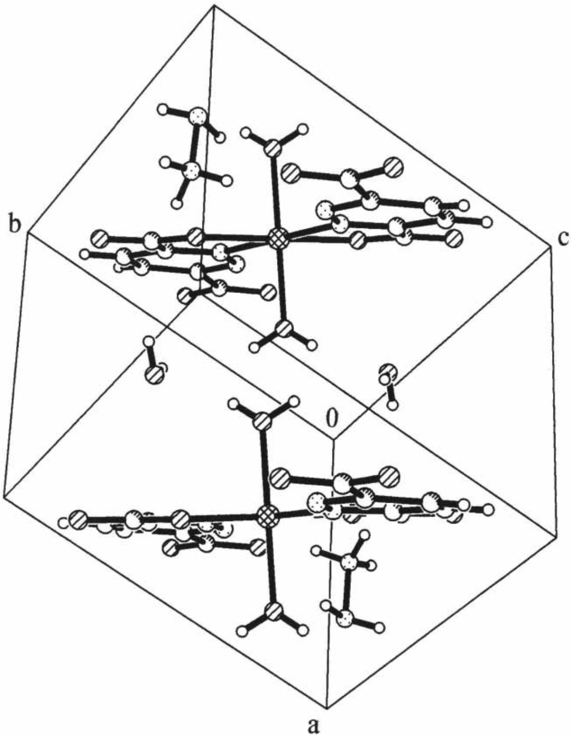

FIGURE 2 The packing diagram for $(H_2N{\cdot}NH_3)^+{}_2[Mg(3,6\text{-PRDC})_2(H_2O)_2]^{2-}{\cdot}2H_2O$.

Only two structures of 3,6-PRDC complexes with divalent metals have been reported previously. The Mn(II) complex shows a very similar coordination mode to that observed in the title compound: monomeric molecules $Mn[H_2(3,6\text{-PRDC})_2(H_2O)_2]$ [8]. On the other hand, dimeric molecular assemblies $Ni_2(3,6\text{-PRDC})_2(H_2O)_4$, formed by two Ni(II) ions bridged by two ligand molecules that use their N,O bonding moieties, have been reported in the structure of the nickel(II) complex [9].

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