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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
H-atom completeness 76%
Disorder in solvent or counterion
 R factor = 0.055
 wR factor = 0.186
Data-to-parameter ratio = 16.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

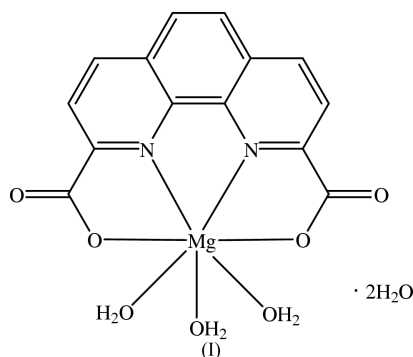
A magnesium(II) complex of 1,10-phenanthroline-2,9-dicarboxylate

The title compound, triaqua(1,10-phenanthroline-2,9-dicarboxylato)magnesium(II) dihydrate, $[\text{Mg}(\text{PDA})(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$, (H_2PDA is 1,10-phenanthroline-2,9-dicarboxylic acid, $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_4$) has twofold crystallographic symmetry. The Mg atom is in a distorted pentagonal bipyramidal coordination environment with two N atoms and two O atoms from PDA and one O atom from a water molecule forming the pentagonal plane, and two O atoms from two water molecules occupying axial positions. The crystal structure comprises an infinite two-dimensional network of hydrogen-bonded molecules.

Received 26 February 2001
Accepted 9 March 2001
Online 16 March 2001

Comment

1,10-Phenanthroline-2,9-dicarboxylic acid (H_2PDA) has been used as a simple sensitizing species of luminescent lanthanide ion chelates for analytical applications in aqueous solution (Sammes & Yahioğlu, 1994; Mullins *et al.*, 1996). However, investigations of H_2PDA complexes with metal ions, such as Fe^{II} and Eu^{II} , have been limited to spectroscopic characterizations in aqueous solution (König & Ritter, 1981; Templeton & Pollak, 1989; Sammes *et al.*, 1992; Dyson *et al.*, 1999). To our knowledge, no examples of Mg^{II} complexes of H_2PDA have been characterized in the solid state. We have prepared the Mg^{II} complex of H_2PDA , (I), and report its crystal structure here.



The title compound (Fig. 1) is located on a twofold axis of symmetry which passes through the Mg and O3 atoms. The seven-coordinated Mg atom is in a distorted pentagonal bipyramidal geometry. Two N and two O atoms from PDA and one O atom from a water molecule define the pentagonal plane, and the two axial positions are occupied by O atoms derived from two water molecules.

Important bond distances and angles are presented in Table 1. The bond distances between Mg and the PDA donor atoms [$\text{Mg}-\text{O}1$ 2.3080 (17) Å and $\text{Mg}-\text{N}1$ 2.2994 (19) Å] are significantly longer than those to the coordinated water mol-

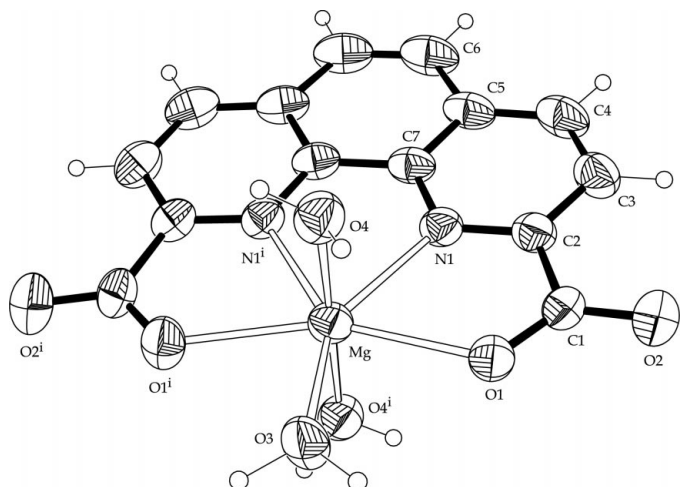


Figure 1
The structure of the title compound with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level (Johnson, 1976). The non-coordinated water molecule has been omitted for clarity. [Symmetry code: (i) $-x + \frac{3}{4}, -y + \frac{3}{4}, z$].

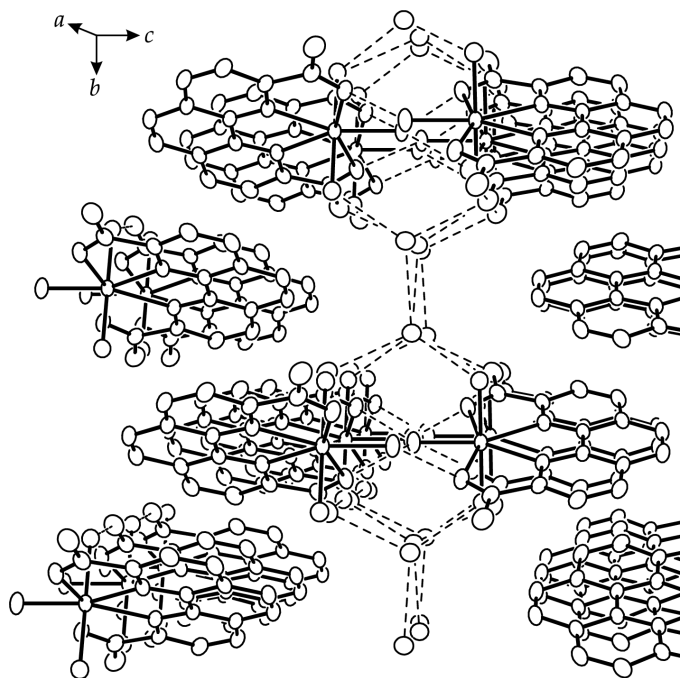


Figure 2
Packing diagram of (I) viewed along [100]. Hydrogen bonds are indicated by dashed lines. Displacement ellipsoids are shown at the 30% probability level. All H atoms and the disordered water molecules with lower site occupancy have been omitted for clarity.

ecules [Mg—O3 2.055 (2) Å and Mg—O4 2.0777 (18) Å]. This is probably due to the high rigidity of PDA as well as the high affinity of the Mg^{II} ion to water molecules. The carboxylate groups of the PDA ligand are almost coplanar with the phenanthroline unit as indicated by the O1—C1—C2—N1 torsion angle of 1.9 (3)°.

The complexes are inter-connected by hydrogen bonds between the coordinated water molecules, O3 and O4, and the

carboxylate O atoms of adjacent PDA with interaction distances of 2.774 (2) and 2.745 (3) Å (Table 2); the equatorial water molecule is hydrogen bonded with the coordinated carboxylate O atoms and the axial water molecules interact with the carbonyl O atoms.

As illustrated in Fig. 2, the complexes associate along the *a* axis and form columns in the crystal structure. Non-coordinated water molecules also participate in hydrogen bonds and serve to connect the complex units along the *b* axis. Stacking interactions between centrosymmetrically related phenanthroline units are observed with a plane-to-plane separation of 3.360 (4) Å.

Experimental

H₂PDA was synthesized according to the literature (König & Ritter, 1981). The title compound was crystallized by slow evaporation from the methanol solution prepared by the reaction of equimolar amounts of H₂PDA and MgSO₄.

Crystal data

[Mg(C₁₄H₆N₂O₄)(H₂O)₃]·2H₂O
M_r = 380.60
 Orthorhombic, *Fddd*
a = 7.4194 (12) Å
b = 19.044 (3) Å
c = 46.943 (7) Å
V = 6632.8 (18) Å³
Z = 16
D_x = 1.525 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 10406 reflections
 θ = 1.7–28.3°
 μ = 0.16 mm⁻¹
T = 293 (2) K
 Plate, yellow
 0.20 × 0.20 × 0.15 mm

Data collection

CCD area detector diffractometer
 φ and ω scans
 10 406 measured reflections
 2063 independent reflections
 1385 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.066
 θ_{\max} = 28.3°
h = −9 → 9
k = −25 → 25
l = −62 → 42

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.055
wR(*F*²) = 0.186
S = 1.06
 2063 reflections
 129 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1026P)^2 + 8.6902P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Mg—O3	2.055 (2)	Mg—N1	2.2994 (19)
Mg—O4	2.0777 (18)	Mg—O1	2.3080 (17)
O3—Mg—O4	89.81 (5)	O3—Mg—O1	77.65 (5)
O4 ⁱ —Mg—O4	179.63 (11)	O4—Mg—O1	87.41 (7)
O4—Mg—N1	89.28 (7)	N1—Mg—O1	68.04 (6)
N1—Mg—N1 ⁱ	68.64 (10)		

Symmetry codes: (i) $\frac{3}{4} - x, \frac{3}{4} - y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3A···O1 ⁱ	0.991 (1)	1.791 (2)	2.774 (2)	170.6 (1)
O4—H4A···O2 ⁱⁱ	0.856 (2)	1.891 (2)	2.745 (3)	175.8 (1)
O4—H4B···O5	0.922 (2)	1.960 (7)	2.863 (6)	165.7 (4)
O4—H4B···O5'	0.922 (2)	1.89 (1)	2.80 (1)	169 (2)
O5···O2 ⁱⁱⁱ			2.866 (7)	
O5'···O2 ⁱⁱⁱ			2.71 (2)	
O5···O5 ^{iv}			2.84 (1)	
O5'···O5 ^{iv}			2.73 (3)	

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{4} - y, \frac{1}{4} - z$; (ii) $x - 1, y, z$; (iii) $\frac{5}{4} - x, y, \frac{1}{4} - z$; (iv) $x, \frac{5}{4} - y, \frac{1}{4} - z$.

The C—H atoms were added at their calculated positions [$U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$] and refined using a riding model. The H atoms of the coordinated water molecules were located from a difference map but were not refined. The non-coordinated water molecule, O5, is disordered over two sites with occupancies of 0.7 for O5 and 0.3 for O5'; H atoms were not included for this molecule.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXTL* (Siemens, 1996); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The support of the Korea Research Foundation (99-005-D00004) is gratefully acknowledged.

References

- Dyson, R. M., Lawrance, G. A., Mäcke, H. & Maeder, M. (1999). *Polyhedron*, **18**, 3243–3251.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- König, E. & Ritter, G. (1981). *J. Inorg. Nucl. Chem.* **43**, 2273–2280.
- Mullins, S. T., Sannes, P. G., West, R. M. & Yahioglu, G. (1996). *J. Chem. Soc. Perkin Trans. I*, pp. 75–81.
- Sannes, P. G. & Yahioglu, G. (1994). *Chem. Soc. Rev.* pp. 327–334.
- Sannes, P. G., Yahioglu, G. & Yearwood, G. D. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1282–1283.
- Siemens (1996), *SMART*, *SAINT* (Version 4.0) and *SHELXTL* (Version 5.03). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Templeton, E. F. G. & Pollak, A. (1989). *J. Lumin.* **43**, 195–205.