Poly[[diaquabis[\(\mu\)-2-(4-fluorophenoxy)acetato-\(\kappa^2O^1:O^1'\)]magnesium]\(0.4\)-hydrate]

Graham Smith

*Acta Cryst.* (2012). E68, m1178

This open-access article is distributed under the terms of the Creative Commons Attribution Licence http://creativecommons.org/licenses/by/2.0/uk/legalcode, which permits unrestricted use, distribution, and reproduction in any medium, provided the original authors and source are cited.

*Acta Crystallographica Section E: Structure Reports Online* is the IUCr’s highly popular open-access structural journal. It provides a simple and easily accessible publication mechanism for the growing number of inorganic, metal-organic and organic crystal structure determinations. The electronic submission, validation, refereeing and publication facilities of the journal ensure very rapid and high-quality publication, whilst key indicators and validation reports provide measures of structural reliability. The journal publishes over 4000 structures per year. The average publication time is less than one month.
Poly[[diaquabis[µ-2-(4-fluorophenoxy)acetoxy]-κ²O¹:O¹']magnesium] 0.4-hydrate]

Graham Smith

Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia
Correspondence e-mail: g.smith@qut.edu.au

Received 31 July 2012; accepted 9 August 2012

In the title compound, [[Mg(C₈H₆FO₃)₂(H₂O)₂]·0.4H₂O]ₙ, slightly distorted octahedral MgO₆ complex units have crystallographic inversion symmetry, the coordination polyhedron comprising two trans-related water molecules and four carboxyl O-atom donors, two of which are bridging. Within the two-dimensional complex polymer which is parallel to (100), coordinating water molecules form intermolecular O—H···O hydrogen bonds with carboxylate and phenoxo O-atom acceptors, as well as with the partial-occupancy solvent water molecules.

Related literature

For the structures of some magnesium complexes, derived from phenoxyacetic acids, see: Smith et al. (1980, 1981, 1982); Kennard et al. (1986). For the structures of other metal complexes with 4-fluorophenoxyacetate, see: O’Reilly et al. (1984); Smith et al. (1993).

Experimental

Crystal data

V = 893.57 (7) Å³
Z = 2
Mo Kα radiation
μ = 0.17 mm⁻¹
T = 200 K
0.30 × 0.20 × 0.05 mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2012)
Tmin = 0.964, Tmax = 0.980
5825 measured reflections
1762 independent reflections
1400 reflections with I > 2σ(I)
Rint = 0.040

Refinement

R[F² > 2σ(F²)] = 0.047
wR(F²) = 0.109
S = 1.06
1762 reflections
133 parameters
H-atom parameters constrained
Δρmax = 0.25 e Å⁻³
Δρmin = -0.29 e Å⁻³

Table 1

Selected bond lengths (Å).

Table 2

Hydrogen-bond geometry (Å, °).

Data collection: CrysAlis PRO (Agilent, 2012); cell refinement: CrysAlis PRO; data reduction: CrysAlis PRO; program(s) used to solve structure: SIR92 (Altomare et al., 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 1999); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON.

The author acknowledges financial support from the Australian Research Council, the Science and Engineering Faculty and the University Library, Queensland University of Technology.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5512).

References

Agilent (2012). CrysAlis PRO. Agilent Technologies Ltd, Yarnton, England.
Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). J. Appl. Cryst. 26, 343–350.
Farrugia, L. J. (1999). J. Appl. Cryst. 32, 837–838.
Kennard, C. H. L., O’Reilly, E. J., Schiller, S., Smith, G. & White, A. H. (1986). Aust. J. Chem. 39, 1823–1832.
O’Reilly, E. J., Smith, G. & Kennard, C. H. L. (1984). Inorg. Chim. Acta, 90, 63–71.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
Smith, G., Lynch, D. E., Mak, T. C. W., Yip, W.-H. & Kennard, C. H. L. (1993). Polyhedron, 12, 203–208.
Smith, G., O’Reilly, E. J. & Kennard, C. H. L. (1980). J. Chem. Soc. Dalton Trans. pp. 2462–2466.
Smith, G., O’Reilly, E. J. & Kennard, C. H. L. (1981). Cryst. Struct. Commun. 10, 1397–1402.
Smith, G., O’Reilly, E. J. & Kennard, C. H. L. (1982). Inorg. Chim. Acta, 62, 241–246.
Spek, A. L. (2009). Acta Cryst. D65, 148–155.

m1178 Graham Smith
supplementary materials

Acta Cryst. (2012). E68, m1178   [doi:10.1107/S1600536812035246]

Poly[[diaquabis[µ-2-(4-fluorophenoxy)acetato-κ²O₁:O¹]magnesium] 0.4-hydrate]

Graham Smith

Comment
Magnesium complexes involving monoanionic phenoxyacetate ligands (L) show a variety of coordination modes, all based on an octahedral MgO₆ metal stereochemistry, e.g. discrete monomeric [[MgL₂(H₂O)₄] (L = 2-fluorophenoxyacetate) (Kennard et al., 1986); (L = 4-chloro-2-methylphenoxyacetate) (Smith et al., 1981); [MgL(H₂O)] (L = 2,4,5-trichlorophenoxyacetate) (Smith et al., 1982)], or polymeric [[MgL₂(H₂O)₄] (L = phenoxyacetate or 4-chlorophenoxyacetate) (Smith et al., 1980)].

The title complex, [Mg(H₂O)₂(C₈H₆FO₃)₂]ₙ (0.4H₂O)ₙ was obtained from the reaction of 4-fluorophenoxyacetic acid with MgCO₃ in aqueous ethanol and the structure is reported herein. In this structure (Fig. 1), the slightly distorted octahedral MgO₆ complex units [bond range Mg—O, 2.0478 (14)–2.1032 (14) Å (Table 1)] have crystallographic inversion symmetry, the coordination polyhedron comprising two trans-related water molecules and four carboxyl O-atom donors, two of which are bridging. Within the two-dimensional complex polymer layers which extend across (100), the coordinated water molecules from intermolecular O—H···O hydrogen-bonding interactions (Table 2), with carboxyl and phenoxy O-atom acceptors as well as with the partial water molecules of solvation (S.O.F. = 0.2) (Fig. 2). Except for the presence of the partial water molecules, the structure is similar to the those of the isomorphous Mg complexes with phenoxyacetate and 4-chlorophenoxyacetate (Smith et al., 1980). In the present complex, the 4-fluorophenoxyacetate ligand is essentially planar, with the carboxyl group rotated slightly out of the plane [benzene ring to acetate dihedral angle = 12.26 (12)°].

Experimental
The title compound was synthesized by the addition of excess MgCO₃ to 15 ml of a hot aqueous ethanolic solution (10:1) of 4-fluorophenoxyacetic acid (0.1 g). After completion of the reaction, the excess MgCO₃ was removed by filtration and the solution was allowed evaporate to incipient dryness at room temperature, giving thin colourless plates of the title compound from which a specimen was cleaved for the X-ray analysis.

Refinement
Hydrogen atoms on the coordinated water molecule were located by difference methods and both positional and isotropic displacement parameters were initially refined but these were then allowed to ride, with \(U_{iso}(H) = 1.5U_{eq}(C)\). Other H-atoms were included in the refinement at calculated positions [C—H(aromatic) = 0.93 Å, 0.98 Å (methylene)] or O—H = 0.84–0.94 Å, with \(U_{iso}(H) = 1.2U_{eq}(C)\) or \(1.5U_{eq}(O)\), also using a riding-model approximation. The site occupancy factor for the partial water molecule of solvation was determined as 0.196 (4) and was subsequently fixed as 0.20.
Computing details
Data collection: CrysAlis PRO (Agilent, 2012); cell refinement: CrysAlis PRO (Agilent, 2012); data reduction: CrysAlis PRO (Agilent, 2012); program(s) used to solve structure: SIR92 (Altomare et al., 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 1999); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON (Spek, 2009).

Figure 1
The molecular structure of the title compound, including the partial water molecules of solvation (O2W), with displacement ellipsoids drawn at the 50% probability level. For symmetry codes, see Table 1.

Figure 2
The hydrogen-bonding interactions, shown as dashed lines, in the title compound viewed along c. The partial water molecule of solvation and non-associative H-atoms have been omitted. For symmetry codes, see Tables 1 and 2.
Poly[[diaquabis[μ-2-(4-fluorophenoxy)acetato-κ2O′:O′]magnesium] 0.4-hydrate]

Crystal data

\[ \text{[Mg(C_8H_6FO_3)_2(H_2O)_2]} \cdot 0.4\text{H}_2\text{O} \]

\[ M_r = 405.80 \]

Monoclinic, \( P2_1/c \)

Hall symbol: -P 2ybc

\( a = 17.2526 \) (9) Å

\( b = 6.8899 \) (3) Å

\( c = 7.5474 \) (3) Å

\( \beta = 95.118 \) (4)°

\( V = 893.57 \) (7) Å³

\( Z = 2 \)

Data collection

Oxford Diffraction Gemini-S CCD-detector

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels mm⁻¹

\( \theta = 3.2–28.9^\circ \)

\( \mu = 0.17 \) mm⁻¹

\( T = 200 \) K

Plate, colourless

\( 0.30 \times 0.20 \times 0.05 \) mm

\( 5825 \) measured reflections

\( 1762 \) independent reflections

Refinement

Refinement on \( F^2 \)

Secondary atom site location: difference Fourier map

Refinement on \( F \) against ALL reflections

Hydrogen site location: inferred from neighbouring sites

\( \Delta \rho_{\text{max}} = 0.25 \) e Å⁻³

\( \Delta \rho_{\text{min}} = -0.29 \) e Å⁻³

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of \( F^2 \) against ALL reflections. The weighted \( R \)-factor \( wR \) and goodness of fit \( S \) are based on \( F^2 \), conventional \( R \)-factors \( R \) are based on \( F \), with \( F \) set to zero for negative \( F^2 \). The threshold expression of \( F^2 > \sigma(F^2) \) is used only for calculating \( R \)-factors(gt) etc. and is not relevant to the choice of reflections for refinement. \( R \)-factors based on \( F^2 \) are statistically about twice as large as those based on \( F \), and \( R \)-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x     | y     | z     | \( U_{\text{int}} \)/\( U_{\text{eq}} \) | Occ. (<1) |
|----|-------|-------|-------|---------------------------------|-----------|
| Mg1 | 0.00000 | 0.50000 | 0.50000 | 0.0187 (3) |           |
| F4  | 0.49577 (8) | -0.0237 (3) | 0.7819 (2) | 0.0567 (6) |           |
| O1  | 0.20100 (10) | -0.0103 (3) | 0.4489 (2) | 0.0481 (6) |           |
| O1W | 0.09125 (8) | 0.6177 (2) | 0.36712 (19) | 0.0255 (5) |           |
| O21 | 0.01967 (8) | 0.2303 (2) | 0.39916 (19) | 0.0255 (4) |           |
supplementary materials

|     | U^21  | U^22  | U^23  | U^31  | U^32  | U^33  |
|-----|-------|-------|-------|-------|-------|-------|
| Mg1 | 0.0232 (5) | 0.0158 (5) | 0.0167 (5) | 0.0015 (4) | 0.0003 (4) | -0.0012 (4) |
| F4  | 0.0271 (7) | 0.0734 (12) | 0.0671 (11) | 0.0020 (8) | -0.0101 (7) | 0.0008 (9) |
| O1  | 0.0388 (10) | 0.0607 (12) | 0.0412 (11) | 0.0274 (9) | -0.0169 (8) | -0.0299 (9) |
| O1W | 0.0299 (8) | 0.0252 (8) | 0.0249 (8) | 0.0015 (7) | 0.0008 (6) | 0.0034 (6) |
| O21 | 0.0297 (8) | 0.0197 (7) | 0.0261 (8) | 0.0051 (7) | -0.0011 (6) | -0.0065 (6) |
| O22 | 0.0274 (8) | 0.0198 (7) | 0.0186 (7) | 0.0013 (6) | 0.0003 (6) | -0.0028 (6) |
| C1  | 0.0310 (12) | 0.0464 (15) | 0.0286 (13) | 0.0124 (12) | -0.0048 (10) | -0.0082 (11) |
| C2  | 0.0461 (16) | 0.0655 (19) | 0.0416 (16) | 0.0250 (15) | -0.0107 (13) | -0.0223 (14) |
| C3  | 0.0373 (15) | 0.0621 (18) | 0.0457 (16) | 0.0206 (14) | -0.0021 (12) | -0.0062 (14) |
| C4  | 0.0249 (12) | 0.0519 (16) | 0.0401 (15) | -0.0001 (12) | -0.0021 (11) | 0.0062 (13) |
| C5  | 0.0354 (14) | 0.0475 (16) | 0.0383 (15) | -0.0048 (12) | -0.0037 (11) | -0.0096 (12) |
| C6  | 0.0334 (13) | 0.0466 (15) | 0.0327 (13) | 0.0060 (12) | -0.0012 (11) | -0.0109 (12) |
| C11 | 0.0293 (12) | 0.0258 (11) | 0.0237 (11) | 0.0069 (10) | -0.0005 (9) | -0.0071 (9) |
| C21 | 0.0254 (11) | 0.0130 (9) | 0.0198 (10) | -0.0022 (9) | 0.0022 (8) | 0.0013 (8) |
| O2W | 0.045 (5) | 0.054 (6) | 0.043 (5) | -0.017 (5) | 0.001 (4) | 0.009 (4) |

Geometric parameters (Å, °)

| Bond | Distance (Å) | Angle (°) |
|------|--------------|-----------|
| Mg1—O1W | 2.1032 (14) | 1.9500 |
| Mg1—O21 | 2.0478 (14) | 1.384 (4) |
| Mg1—O22 | 2.0620 (14) | 1.379 (3) |
| Mg1—O1W* | 2.1032 (14) | 1.381 (4) |
| Mg1—O21* | 2.0478 (14) | 1.356 (4) |
| Mg1—O22* | 2.0620 (14) | 1.363 (4) |
| F4—C4 | 1.362 (3) | 1.390 (3) |

Acta Cryst. (2012). E68, m1178
supplementary materials

| Bond             | Length (Å) | Symmetry Code          | Angle (°) | Symmetry Code          | Length (Å) |
|------------------|------------|------------------------|-----------|------------------------|------------|
| O1—C1            | 1.380 (3)  | C1—C2—C3              | 120.3 (3) | C1—C2—C3              | 1.511 (3)  |
| O1—C11           | 1.416 (3)  | C2—H2                 | 0.930     | C2—H2                 | 0.930      |
| O21—C21          | 1.257 (3)  | C3—H3                 | 0.930     | C3—H3                 | 0.930      |
| O22—C21          | 1.250 (3)  | C5—H5                 | 0.930     | C5—H5                 | 0.930      |
| O1W—H11W         | 0.9100     | C6—H6                 | 0.970     | C6—H6                 | 0.970      |
| O1W—H12W         | 0.9200     | C11—H11B              | 0.970     | C11—H11B              | 0.970      |
| O2W—H22W         | 0.8500     | C11—H11A              | 0.970     | C11—H11A              | 0.970      |
| O1W—Mg1—O21      | 90.96 (5)  | C1—C2—C3              | 120.3 (3) | C1—C2—C3              | 1.511 (3)  |
| O1W—Mg1—O22i     | 92.03 (5)  | C2—C3—C4              | 118.7 (2) | C2—C3—C4              | 118.7 (2)  |
| O1W—Mg1—O1Wi     | 180.00     | F4—C4—C3              | 118.7 (2) | F4—C4—C3              | 118.7 (2)  |
| O1W—Mg1—O21i     | 89.04 (5)  | F4—C4—C5              | 118.7 (2) | F4—C4—C5              | 118.7 (2)  |
| O1W—Mg1—O22ii    | 87.97 (5)  | C3—C4—C5              | 122.6 (2) | C3—C4—C5              | 122.6 (2)  |
| O21—Mg1—O22i     | 84.33 (5)  | C4—C5—C6              | 119.0 (2) | C4—C5—C6              | 119.0 (2)  |
| O1W—Mg1—O21      | 89.04 (5)  | C1—C6—C5              | 119.6 (2) | C1—C6—C5              | 119.6 (2)  |
| O21—Mg1—O21a     | 180.00     | O1—C11—C21            | 109.90 (17) | O1—C11—C21            | 109.90 (17) |
| O21—Mg1—O21b     | 95.67 (5)  | O21—C21—C11           | 115.38 (19) | O21—C21—C11           | 115.38 (19) |
| O21—Mg1—O22b     | 87.97 (5)  | O22—C21—C11           | 119.32 (18) | O22—C21—C11           | 119.32 (18) |
| O21—Mg1—O22c     | 95.67 (5)  | O21—C21—O22           | 125.3 (2)  | O21—C21—O22           | 125.3 (2)  |
| O21—Mg1—O22d     | 180.00     | C3—C2—H2              | 120.00    | C3—C2—H2              | 120.00     |
| O21—Mg1—O21a     | 90.96 (5)  | C1—C2—H2              | 120.00    | C1—C2—H2              | 120.00     |
| O21—Mg1—O21b     | 92.03 (5)  | C2—C3—H3              | 121.00    | C2—C3—H3              | 121.00     |
| C1—O1—C11        | 117.06 (19)| C4—C5—H5              | 120.00    | C4—C5—H5              | 120.00     |
| Mg1—O21—C21      | 139.08 (14)| C6—C5—H5              | 121.00    | C6—C5—H5              | 121.00     |
| Mg1—O21—C21      | 132.00 (13)| C5—C6—H6              | 120.00    | C5—C6—H6              | 120.00     |
| Mg1—O1W—H12W     | 103.00     | C1—C6—H6              | 120.00    | C1—C6—H6              | 120.00     |
| H11W—O1W—H12W    | 114.00     | O1—C11—H11A           | 110.00    | O1—C11—H11A           | 110.00     |
| Mg1—O1W—H11W     | 123.00     | O1—C11—H11B           | 110.00    | O1—C11—H11B           | 110.00     |
| H21W—O2W—H22W    | 102.00     | C21—C11—H11B          | 110.00    | C21—C11—H11B          | 110.00     |
| O1—C1—C6         | 124.9 (2)  | H11A—C11—H11B         | 108.00    | H11A—C11—H11B         | 108.00     |
| C2—C1—C6         | 119.9 (2)  | C21—C11—H11A          | 110.00    | C21—C11—H11A          | 110.00     |
| O1—C1—C2         | 115.2 (2)  | C21—C11—H11A          | 110.00    | C21—C11—H11A          | 110.00     |
| O1W—Mg1—O21—C21  | 36.0 (2)   | C6—C1—C2—C3           | −0.2 (4)  | C6—C1—C2—C3           | −0.2 (4)   |
| O22—Mg1—O21—C21  | 127.9 (2)  | O1—C1—C6—C5           | −179.4 (2) | O1—C1—C6—C5           | −179.4 (2) |
| O1W—Mg1—O21—C21  | −144.0 (2) | C2—C1—C6—C5           | −0.3 (4)  | C2—C1—C6—C5           | −0.3 (4)   |
| O22—Mg1—O21—C21  | −52.1 (2)  | C1—C2—C3—C4           | 0.7 (4)   | C1—C2—C3—C4           | 0.7 (4)    |
| C11—O1—C1—C2     | −175.1 (2) | C2—C3—C4—F4           | 178.5 (2) | C2—C3—C4—F4           | 178.5 (2)  |
| C11—O1—C1—C6     | 4.0 (3)    | C2—C3—C4—C5           | −0.7 (4)  | C2—C3—C4—C5           | −0.7 (4)   |
| C1—O1—C1—C11     | 169.15 (19)| F4—C4—C5—C6           | −179.0 (2)| F4—C4—C5—C6           | −179.0 (2) |
| Mg1—O21—C21—O22  | −136.10 (18)| C3—C4—C5—C6           | 0.2 (4)   | C3—C4—C5—C6           | 0.2 (4)    |
| Mg1—O21—C21—C11  | 43.1 (3)   | C4—C5—C6—C1           | 0.3 (4)   | C4—C5—C6—C1           | 0.3 (4)    |
| Mg1—O22—C21—O21  | 4.0 (3)    | O1—C11—C21—O21        | 172.84 (18) | O1—C11—C21—O21        | 172.84 (18) |
| Mg1—O22—C21—C11  | −175.24 (13)| O1—C11—C21—O22        | −7.9 (3)  | O1—C11—C21—O22        | −7.9 (3)   |

Symmetry codes: (i) −x, y+1/2, −z+1/2; (ii) −x, −y+1, −z+1; (iii) x, −y+1/2, z+1/2; (iv) −x, −y−1/2, −z+1/2.
Hydrogen-bond geometry (Å, °)

| D—H···A       | D—H | H···A | D···A      | D—H···A |
|---------------|-----|-------|------------|---------|
| O1W—H11W···O1v | 0.91| 2.45  | 3.214 (2)  | 143     |
| O1W—H12W···O22v| 0.92| 2.38  | 3.0352 (19)| 128     |
| O1W—H12W···O21i| 0.92| 1.92  | 2.760 (2)  | 151     |
| O2W—H21W···O1v | 0.95| 2.41  | 3.034 (10) | 123     |
| O2W—H22W···O22iii| 0.85| 2.13  | 2.950 (9)  | 160     |

Symmetry codes: (i) −x, y+1/2, −z+1/2; (iii) x, −y+1/2, z+1/2; (v) x, y+1, z.