Crystal structure of the magnesium salt of the herbicide 2,4-D: pentaaqua[(2,4-dichlorophenoxy)acetato-κO]magnesium (2,4-dichlorophenoxy)acetate hemihydrate

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Crystal structure of the magnesium salt of the herbicide 2,4-D: pentaaqua[(2,4-dichlorophenoxy)acetato-κO]magnesium (2,4-dichlorophenoxy)acetate hemihydrate

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

In the crystal structure of the title magnesium salt of the phenoxy herbicide (2,4-dichlorophenoxy)acetic acid (2,4-D), \(\text{[Mg}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)(\text{H}_2\text{O})_5]\text{[C}_8\text{H}_5\text{Cl}_2\text{O}_3]/\text{Cl}_2\text{O}_3\cdot0.5\text{H}_2\text{O}\), the discrete cationic \(\text{MgO}_6\) complex unit comprises a carboxylate O-donor from a monodentate 2,4-D anionic ligand and five water molecules, resulting in a slightly distorted octahedral coordination sphere. The free 2,4-D anions are linked to the complex units through duplex water–carboxylate O—H···O hydrogen bonds through the coordinating water molecules. In the crystal, inter-unit O—H···O hydrogen-bonding interactions involving coordinating water molecules as well as the solvent water molecule (occupancy 0.5) with carboxylate O-atom acceptors, give a layered structure lying parallel to (001), in which \(\pi\)–\(\pi\) ligand–cation interactions [minimum ring centroid separation = 3.6405 (17) Å] and a short O—H···Cl interaction are also found.

1. Chemical context

The phenoxyacetic acids comprise an important group of chemicals which has among its members those ring-substituted representatives having selective herbicidal activity, e.g. the commercial but in some cases, now prohibited (2,4-dichlorophenoxy)acetic acid (2,4-D), (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) and (4-chloro-2-methylphenoxy)acetic acid (MCPA) (O’Neill, 2002; Zumdahl, 2010; Cobb & Reade, 2011). Of interest have also been the structures of the metal complexes with these acids, including those with magnesium in which the monoanionic phenoxyacetate ligands \(L\) display a variety of coordination modes, all based on an octahedral \(\text{MgO}_6\) metal stereochemistry. These include discrete monomeric \([\text{MgL}_2(\text{H}_2\text{O})_6]\) \([L = 2\text{-}(2\text{-fluorophenoxy})acetate\] (Kennard et al., 1986) and \(L = \text{MCPA}^-\) (Smith et al., 1981)] and \([\text{MgL}(\text{H}_2\text{O})_3]_2\) \([L = 2\text{-}(2\text{-fluorophenoxy})acetate\] or \([\text{MgL}(\text{H}_2\text{O})_3]_2\) \([L = \text{phenoxyacetate, (4-chlorophenoxy)acetate or (4-fluorophenoxy)acetate}\) (Smith et al., 1980; Smith, 2012)]. The title complex, \([\text{Mg}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)\cdot(\text{H}_2\text{O})_3](\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)\cdot0.5\text{H}_2\text{O}\), was obtained from the reaction of 2,4-D with MgCO\(_3\) in aqueous ethanol and its crystal structure is reported herein.
2. Structural commentary

In the title complex (Fig. 1), the discrete MgO₆ complex units have, as expected, essentially octahedral stereochemistry [Mg—O bond length range = 2.031 (2)–2.094 (2) \(\text{Å}\)], comprising a carboxylate O-donor from a monodentate 2,4-D⁻ ligand and five water molecules. The free 2,4-D⁻ counterion is linked to the complex unit through an unusual duplex water–carboxylate O—H···O hydrogen-bonding association involving the coordinating water molecules O1W and O2W (Table 1), giving a cyclic ring motif incorporating the Mg²⁺ cation [graph set \(R_2^2(8)\)]. Except for the presence of the hemihydrate molecule of solvation, the title complex is very similar to that of the Mg complex with the analogous phenoxy herbicide, (2,4,5-trichlorophenoxy)acetic acid (Smith et al., 1982).

In the present complex, both 2,4-D species are essentially planar [defining torsion angles for the oxoacetic acid side chain (C1A/B—O11A/B—C12A/B—C13A/B and O11A/B—C12A/B—C13A/B—O14A/B) being 179.0 (2) and 174.8 (2)° (ligand A), and 175.7 (2) and 178.7 (2)° (anion B), respectively]. This contrasts with the parent acid 2,4-D (Smith et al., 1976), in which the oxoacetic acid side chain adopts a synclinal conformation (benzene ring to carboxyl group dihedral angle = 75.2°).

3. Supramolecular features

In the crystal of the title compound, inter-unit O—H···O hydrogen-bonding interactions (Table 1) involving all coordinating water molecules, as well as the hemihydrate solvent molecule, with carboxylate O-atom acceptors, give a layered structure lying parallel (001) (Fig. 2). Within these layers, weak π···π interactions between centrosymmetrically related 2,4-D ligand–anion species \(A' \cdots B'\) are also found. The 2,4-D⁻ molecules lie parallel to (10\(\bar{1}\)) and have a minimum ring centroid.

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|------|-------|---------|
| O1W—H11W···O13B | 0.86 (3) | 1.92 (3) | 2.772 (3) | 171 (3) |
| O1W—H12W···O4W\(^1\) | 0.87 (3) | 2.09 (3) | 2.939 (3) | 165 (3) |
| O2W—H21W···O14B | 0.88 (2) | 1.75 (2) | 2.623 (3) | 176 (3) |
| O2W—H22W···O14B\(^1\) | 0.87 (3) | 1.88 (3) | 2.754 (3) | 173 (3) |
| O3W—H31W···O13A\(^1\) | 0.87 (2) | 1.80 (2) | 2.656 (3) | 167 (3) |
| O3W—H32W···O12A\(^1\) | 0.87 (3) | 2.30 (3) | 3.345 (2) | 165 (3) |
| O4W—H11W···O13A\(^1\) | 0.89 (2) | 1.77 (2) | 2.652 (3) | 172 (4) |
| O4W—H42W···O2W\(^2\) | 0.88 (2) | 2.19 (3) | 2.980 (3) | 151 (3) |
| O5W—H51W···O6W\(^1\) | 0.90 (5) | 1.90 (6) | 2.543 (5) | 127 (4) |
| O5W—H52W···O13B\(^2\) | 0.88 (4) | 1.86 (4) | 2.708 (4) | 162 (4) |
| O6W—H61W···O14B\(^2\) | 0.91 (6) | 1.77 (6) | 2.654 (5) | 162 (7) |
| O6W—H62W···O14A | 0.90 (6) | 2.12 (5) | 3.006 (5) | 168 (5) |

Symmetry codes: (i) \(x + 1, y + 1, z + 1\); (ii) \(x + 1, y, z + 1\); (iii) \(x, y, z\); (iv) \(x + 1, y, z + 1\); (v) \(x + 1, y, z\); (vi) \(x + 2, y, z + 1\); (vii) \(x + 1, y, z + 1\).
separation of 3.6405 (17) Å. A short O3W—H· · ·C12A\textsuperscript{iii} interaction [3.345 (2) Å] is also observed [for symmetry codes (i) and (iii), see: Table 1].

4. Synthesis and crystallization

The title compound was synthesized by the addition of excess MgCO\textsubscript{3} to 15 ml of a hot aqueous solution of (2,4-dichlorophenoxy)acetic acid (0.1 mmol) in ethanol–water (1:10 v/v). After completion of the reaction, excess MgCO\textsubscript{3} was removed by filtration and the solution was allowed to evaporate at room temperature, providing colourless prisms of the title compound from which a specimen was cleaved for the X-ray analysis.

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms on all water molecules were located in difference Fourier maps. Their positional parameters were refined with restraints [O—H = 0.90 (2) Å], with $U_{iso}(H) = 1.5U_{eq}(O)$. Other H atoms were included in the refinement at calculated positions (aromatic C—H = 0.95 Å or methylene 0.99 Å), with $U_{iso}(H) = 1.2U_{eq}(C)$, using a riding-model approximation. The site-occupancy factor for the water molecule of solvation was determined as 0.502 (4) and was subsequently fixed at 0.50.

Acknowledgements

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Computing details

Data collection: CrysAlis PRO (Agilent, 2013); cell refinement: CrysAlis PRO (Agilent, 2013); data reduction: CrysAlis PRO (Agilent, 2013); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) within WinGX (Farrugia, 2012); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON (Spek, 2009).

Pentaaqua[(2,4-dichlorophenoxy)acetato-κO]magnesium (2,4-dichlorophenoxy)acetate hemihydrate

Crystal data

\[ \text{[Mg(C}_8\text{H}_5\text{Cl}_2\text{O}_3)(\text{H}_2\text{O})_5](\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3) \cdot 0.5\text{H}_2\text{O}} \]

\( M_r = 563.44 \)

Triclinic, \( P\bar{1} \)

Hall symbol: -\( P\bar{1} \)

\( a = 7.3551\ (6) \) Å

\( b = 7.6579\ (5) \) Å

\( c = 20.7878\ (14) \) Å

\( \alpha = 91.266\ (6) ^\circ \)

\( \beta = 94.341\ (6) ^\circ \)

\( \gamma = 94.250\ (6) ^\circ \)

\( V = 1163.84\ (14) \) Å³

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Radiation source: Enhance (Mo) X-ray source

Graphite monochromator

Detector resolution: 16.077 pixels mm⁻¹

\( \omega \) scans

Absorption correction: multi-scan \( (\text{CrysAlis PRO}; \text{Agilent, 2013}) \)

\( T_{\text{min}} = 0.970, T_{\text{max}} = 0.980 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.050 \)

\( wR(F^2) = 0.107 \)

\( S = 1.04 \)

6763 measured reflections

4575 independent reflections

3458 reflections with \( I > 2\sigma(I) \)

\( R_{\text{int}} = 0.029 \)

\( \theta_{\text{max}} = 26.0 ^\circ, \theta_{\text{min}} = 3.3 ^\circ \)

\( h = -8 \rightarrow 9 \)

\( k = -9 \rightarrow 8 \)

\( l = -16 \rightarrow 25 \)

4575 reflections

334 parameters

12 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

\[ w = 1/\left(\sigma^2(F_0^2) + 0.0344P^2 + 0.6822P\right) \]
where \( P = (F_0^2 + 2F_c^2)/3 \)

\( (\Delta/\sigma)_{\text{max}} = 0.001 \)
\( \Delta \rho_{\text{max}} = 0.69 \text{ eÅ}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.51 \text{ eÅ}^{-3} \)

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       | Uiso* | Ueq | Occ. (<1) |
|-----|---------|---------|---------|-------|-----|-----------|
| Cl2A | 0.32241 | 1.10346 | 0.21550 | 0.0581 |     | 0.0311    |
| Cl4A | 0.09192 | 0.77979 | −0.01112| 0.0416 |     | 0.0272    |
| Mg1  | 0.64072 | 0.28185 | 0.42864 | 0.0392 |     | 0.0272    |
| O1W  | 0.7607  | 0.4533  | 0.50028 | 0.0392 |     | 0.0311    |
| O2W  | 0.7909  | 0.0906  | 0.47054 | 0.0428 |     | 0.0392    |
| O3W  | 0.5253  | 0.0856  | 0.36448 | 0.0384 |     | 0.0311    |
| O4W  | 0.4292  | 0.2243  | 0.48859 | 0.0354 |     | 0.0392    |
| O5W  | 0.8325  | 0.3474  | 0.36472 | 0.0803 |     | 0.0392    |
| O11A | 0.3737  | 0.7518  | 0.26146 | 0.0311 |     | 0.0428    |
| O13A | 0.5235  | 0.7438  | 0.38384 | 0.0394 |     | 0.0392    |
| O14A | 0.4784  | 0.4541  | 0.38457 | 0.0523 |     | 0.0392    |
| C1A  | 0.3065  | 0.7496  | 0.19790 | 0.0269 |     | 0.0392    |
| C2A  | 0.2754  | 0.9101  | 0.17018 | 0.0291 |     | 0.0392    |
| C3A  | 0.2087  | 0.9207  | 0.10640 | 0.0314 |     | 0.0392    |
| C4A  | 0.1726  | 0.7682  | 0.06967 | 0.0299 |     | 0.0392    |
| C5A  | 0.2025  | 0.6081  | 0.09524 | 0.0339 |     | 0.0392    |
| C6A  | 0.2687  | 0.5993  | 0.15926 | 0.0322 |     | 0.0392    |
| C12A | 0.3942  | 0.5832  | 0.28841 | 0.0308 |     | 0.0392    |
| C13A | 0.4716  | 0.5993  | 0.35773 | 0.0322 |     | 0.0392    |
| C12B | 1.16172 | 0.63544 | 0.80594 | 0.0560 |     | 0.0392    |
| C14B | 1.41057 | 0.24035 | 0.99966 | 0.0459 |     | 0.0392    |
| O11B | 1.1112  | 0.3112  | 0.73144 | 0.0377 |     | 0.0392    |
| O13B | 0.9449  | 0.3560  | 0.61359 | 0.0479 |     | 0.0392    |
| O14B | 0.9418  | 0.0723  | 0.58839 | 0.0584 |     | 0.0392    |
| C1B  | 1.1820  | 0.2850  | 0.79283 | 0.0304 |     | 0.0392    |
| C2B  | 1.2150  | 0.4327  | 0.83429 | 0.0324 |     | 0.0392    |
| C3B  | 1.2847  | 0.4191  | 0.89740 | 0.0341 |     | 0.0392    |
| C4B  | 1.3236  | 0.2574  | 0.91982 | 0.0324 |     | 0.0392    |
| C5B  | 1.2948  | 0.1969  | 0.88026 | 0.0354 |     | 0.0392    |
| C6B  | 1.2253  | 0.1242  | 0.81655 | 0.0356 |     | 0.0392    |

Acta Cryst. (2014). E70, 161-163
supporting information

|    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|
| C12B | 1.0691 (4) | 0.1584 (4) | 0.69131 (14) | 0.0375 (11) |    |    |
| C13B | 0.9786 (4) | 0.2045 (5) | 0.62639 (15) | 0.0412 (11) |    |    |
| O6W | 0.1369 (6) | 0.2203 (6) | 0.3500 (2) | 0.0411 (17) | 0.500 |    |
| H3A | 0.18810 | 1.03100 | 0.08830 | 0.0380* |    |    |
| H5A | 0.17800 | 0.50420 | 0.06930 | 0.0410* |    |    |
| H6A | 0.28850 | 0.48840 | 0.17700 | 0.0390* |    |    |
| H11W | 0.828 (4) | 0.423 (5) | 0.5331 (13) | 0.0590* |    |    |
| H12A | 0.47650 | 0.51830 | 0.26280 | 0.0370* |    |    |
| H12W | 0.713 (5) | 0.549 (3) | 0.5108 (17) | 0.0590* |    |    |
| H13A | 0.27360 | 0.51580 | 0.28600 | 0.0370* |    |    |
| H21W | 0.838 (5) | 0.089 (5) | 0.5105 (10) | 0.0640* |    |    |
| H22W | 0.869 (4) | 0.035 (5) | 0.4497 (16) | 0.0640* |    |    |
| H31W | 0.511 (5) | −0.028 (2) | 0.3660 (17) | 0.0580* |    |    |
| H32W | 0.464 (4) | 0.108 (5) | 0.3286 (12) | 0.0580* |    |    |
| H41W | 0.451 (4) | 0.245 (5) | 0.5307 (9) | 0.0530* |    |    |
| H42W | 0.371 (4) | 0.120 (3) | 0.4861 (17) | 0.0530* |    |    |
| H51W | 0.912 (6) | 0.275 (6) | 0.382 (3) | 0.1210* |    |    |
| H52W | 0.900 (6) | 0.447 (4) | 0.363 (2) | 0.1210* |    |    |
| H3B | 1.30550 | 0.52030 | 0.92500 | 0.0410* |    |    |
| H5B | 1.32220 | −0.00140 | 0.89630 | 0.0430* |    |    |
| H6B | 1.20730 | 0.02270 | 0.78900 | 0.0430* |    |    |
| H12B | 0.98600 | 0.07460 | 0.71280 | 0.0450* |    |    |
| H13B | 1.18280 | 0.10110 | 0.68470 | 0.0450* |    |    |
| H61W | 0.126 (10) | 0.131 (7) | 0.378 (3) | 0.0620* | 0.500 |    |
| H62W | 0.230 (7) | 0.296 (7) | 0.365 (3) | 0.0620* | 0.500 |    |

Atomic displacement parameters (Å²)

|    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|
| Cl2A | 0.1102 (8) | 0.0252 (4) | 0.0356 (5) | 0.0087 (5) | −0.0197 (5) | 0.0018 (3) |
| Cl4A | 0.0416 (5) | 0.0557 (5) | 0.0268 (4) | 0.0087 (4) | −0.0071 (3) | 0.0001 (4) |
| Mg1 | 0.0359 (5) | 0.0197 (5) | 0.0251 (5) | −0.0003 (4) | −0.0007 (4) | 0.00002 (4) |
| O1W | 0.0516 (14) | 0.0262 (12) | 0.0373 (13) | 0.0055 (10) | −0.0121 (10) | −0.0075 (10) |
| O2W | 0.0436 (13) | 0.0400 (14) | 0.0434 (14) | 0.0202 (11) | −0.0164 (10) | −0.0166 (11) |
| O3W | 0.0561 (14) | 0.0209 (11) | 0.0348 (13) | 0.0099 (10) | −0.0169 (10) | −0.0010 (10) |
| O4W | 0.0464 (13) | 0.0290 (12) | 0.0309 (12) | 0.0021 (10) | 0.0042 (10) | 0.0036 (10) |
| O5W | 0.082 (2) | 0.095 (3) | 0.0573 (19) | −0.0509 (18) | 0.0218 (16) | −0.0094 (17) |
| O11A | 0.0489 (12) | 0.0209 (10) | 0.0232 (10) | 0.0040 (9) | −0.0023 (8) | 0.0071 (8) |
| O13A | 0.0628 (15) | 0.0246 (12) | 0.0295 (12) | −0.0012 (10) | −0.0020 (10) | 0.0065 (9) |
| O14A | 0.0907 (19) | 0.0218 (12) | 0.0419 (14) | 0.0064 (12) | −0.0159 (12) | 0.0106 (10) |
| C1A | 0.0289 (15) | 0.0283 (16) | 0.0234 (15) | 0.0018 (12) | 0.0010 (11) | 0.0055 (12) |
| C2A | 0.0371 (17) | 0.0261 (16) | 0.0238 (15) | 0.0014 (13) | 0.0007 (12) | 0.0020 (12) |
| C3A | 0.0342 (16) | 0.0314 (17) | 0.0296 (16) | 0.0079 (13) | 0.0013 (12) | 0.0088 (13) |
| C4A | 0.0266 (15) | 0.0413 (18) | 0.0216 (15) | 0.0028 (13) | −0.0005 (11) | 0.0024 (13) |
| C5A | 0.0363 (17) | 0.0318 (17) | 0.0324 (17) | −0.0004 (13) | −0.0006 (13) | −0.0040 (13) |
| C6A | 0.0386 (17) | 0.0265 (16) | 0.0312 (17) | 0.0007 (13) | 0.0016 (13) | 0.0066 (13) |
| C12A | 0.0438 (18) | 0.0188 (15) | 0.0302 (16) | 0.0040 (13) | 0.0015 (13) | 0.0070 (12) |
| C13A | 0.0425 (18) | 0.0249 (16) | 0.0299 (17) | 0.0063 (13) | 0.0025 (13) | 0.0065 (13) |

Acta Cryst. (2014). E70, 161-163

sup-3

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### Geometric parameters (Å, °)

| Bond/Angle | Value (Å, °) |
|------------|-------------|
| Mg1—O1W   | 2.065 (2)   |
| Mg1—O4W   | 2.094 (2)   |
| Mg1—O5W   | 2.053 (3)   |
| Mg1—O14A  | 2.031 (2)   |
| Mg1—O2W   | 2.067 (2)   |
| Mg1—O3W   | 2.076 (2)   |
| Cl2A—C2A  | 1.736 (3)   |
| Cl4A—C4A  | 1.745 (3)   |
| Cl2B—C2B  | 1.734 (3)   |
| Cl4B—C4B  | 1.744 (3)   |
| O11A—C1A  | 1.375 (3)   |
| O11A—C12A | 1.432 (3)   |
| O13A—C13A | 1.243 (4)   |
| O14A—C13A | 1.258 (4)   |
| O1W—H12W  | 0.87 (3)    |
| O1W—H11W  | 0.86 (3)    |
| O2W—H22W  | 0.87 (3)    |
| O2W—H21W  | 0.88 (2)    |
| O3W—H31W  | 0.870 (16)  |
| O3W—H32W  | 0.87 (3)    |
| O4W—H42W  | 0.88 (2)    |
| O4W—H41W  | 0.89 (2)    |
| O5W—H51W  | 0.90 (5)    |
| O5W—H52W  | 0.88 (4)    |
| O11B—C1B  | 1.366 (4)   |
| O11B—C12B | 1.423 (4)   |
| O13B—C13B | 1.235 (4)   |
| O1W—Mg1—O2W | 87.62 (10)  |
| O1W—Mg1—O3W | 173.07 (10) |
| O1W—Mg1—O4W | 87.94 (9)   |

### Supporting Information

| Atom | U1   | U2   | U3   | U12  | U13  | U23  |
|------|------|------|------|------|------|------|
| Cl2B | 0.0899 (7) | 0.0302 (5) | 0.0493 (5) | 0.0140 (4) | 0.0029 (5) | 0.0068 (4) |
| Cl4B | 0.0388 (5) | 0.0653 (6) | 0.0332 (4) | 0.0054 (4) | 0.0018 (3) | 0.0070 (4) |
| O11B | 0.0491 (13) | 0.0354 (13) | 0.0278 (12) | 0.0029 (10) | 0.0017 (9) | 0.0037 (9) |
| O13B | 0.0471 (14) | 0.0538 (16) | 0.0409 (14) | 0.0040 (12) | 0.0052 (10) | 0.0117 (12) |
| O14B | 0.0687 (17) | 0.0742 (19) | 0.0330 (14) | 0.0209 (14) | 0.0021 (11) | 0.0153 (13) |
| C1B  | 0.0288 (16) | 0.0316 (17) | 0.0314 (17) | 0.0016 (13) | 0.0049 (12) | 0.0051 (13) |
| C2B  | 0.0362 (17) | 0.0245 (16) | 0.0380 (18) | 0.0055 (13) | 0.0075 (13) | 0.0051 (13) |
| C3B  | 0.0339 (17) | 0.0333 (18) | 0.0351 (18) | 0.0024 (13) | 0.0040 (13) | 0.0014 (13) |
| C4B  | 0.0259 (16) | 0.0419 (19) | 0.0298 (17) | 0.0047 (13) | 0.0018 (12) | 0.0058 (14) |
| C5B  | 0.0335 (17) | 0.0345 (18) | 0.0389 (18) | 0.0049 (14) | 0.0021 (13) | 0.0091 (14) |
| C6B  | 0.0411 (18) | 0.0278 (17) | 0.0380 (18) | 0.0039 (14) | 0.0017 (13) | 0.0024 (14) |
| C12B | 0.0383 (18) | 0.0406 (19) | 0.0339 (18) | 0.0043 (14) | 0.0042 (13) | 0.0005 (14) |
| C13B | 0.0361 (18) | 0.060 (2)  | 0.0287 (18) | 0.0055 (17) | 0.0094 (13) | −0.0006 (17) |
| O6W  | 0.044 (3)  | 0.032 (3)  | 0.047 (3)  | 0.000 (2)   | 0.003 (2)   | 0.004 (2)   |
supporting information

O1W—Mg1—O5W 93.97 (12) O14A—C13A—C12A 113.2 (3)
O1W—Mg1—O4W 96.53 (10) O13A—C13A—C12A 121.7 (3)
O2W—Mg1—O3W 86.18 (9) O13A—C13A—O14A 125.1 (3)
O2W—Mg1—O4W 90.97 (9) C2A—C3A—H3A 121.00
O2W—Mg1—O5W 93.47 (12) C4A—C3A—H3A 121.00
O2W—Mg1—O14A 175.40 (10) C6A—C5A—H5A 120.00
O3W—Mg1—O4W 89.06 (9) C4A—C5A—H5A 120.00
O3W—Mg1—O5W 89.51 (12) C5A—C6A—H6A 119.00
O3W—Mg1—O14A 89.56 (10) C1A—C6A—H6A 119.00
O4W—Mg1—O3W 175.23 (12) O11A—C12A—H12A 109.00
O4W—Mg1—O14A 87.21 (10) O11A—C12A—H13A 109.00
O5W—Mg1—O14A 88.23 (12) C13A—C12A—H13A 109.00
C1A—O11A—C12A 115.3 (2) H12A—C12A—H13A 108.00
Mg1—O14A—C13A 146.3 (2) C13A—C12A—H12A 109.00
H11W—O1W—H12W 108 (3) O11B—C1B—C2B 117.1 (3)
Mg1—O1W—H11W 124 (3) O11B—C1B—C6B 124.8 (3)
Mg1—O1W—H12W 122 (2) C2B—C1B—C6B 118.0 (3)
H21W—O2W—H22W 102 (3) C12B—C2B—C1B 119.0 (2)
Mg1—O2W—H21W 127 (2) C12B—C2B—C3B 119.6 (2)
Mg1—O2W—H22W 123 (2) C1B—C2B—C3B 121.4 (3)
Mg1—O3W—H31W 134 (2) C2B—C3B—C4B 119.2 (3)
Mg1—O3W—H32W 122 (2) C4B—C4B—C3B 119.2 (2)
H31W—O3W—H32W 103 (3) C14B—C4B—C5B 119.8 (2)
Mg1—O4W—H41W 119 (2) C3B—C4B—C5B 121.0 (3)
Mg1—O4W—H42W 120 (2) C4B—C5B—C6B 119.5 (3)
H41W—O4W—H42W 104 (3) C1B—C6B—C5B 120.8 (3)
H51W—O5W—H52W 103 (4) O11B—C12B—C13B 110.8 (3)
Mg1—O5W—H51W 93 (3) O13B—C13B—C12B 122.0 (3)
Mg1—O5W—H52W 128 (3) O14B—C13B—C12B 113.0 (3)
C1B—O11B—C12B 116.2 (2) O13B—C13B—O14B 125.0 (3)
H61W—O6W—H62W 109 (6) C2B—C3B—H3B 120.00
C2A—C1A—C6A 117.7 (3) C4B—C3B—H3B 120.00
O11A—C1A—C6A 124.6 (3) C4B—C5B—H5B 120.00
O11A—C1A—C2A 117.6 (2) C6B—C5B—H5B 120.00
C12A—C2A—C1A 120.1 (2) C5B—C6B—H6B 120.00
C1A—C2A—C3A 121.7 (3) C1B—C6B—H6B 120.00
C12A—C2A—C3A 118.2 (2) O11B—C12B—H12B 110.00
C2A—C3A—C4A 118.8 (3) O11B—C12B—H13B 109.00
C3A—C4A—C5A 121.1 (3) C13B—C12B—H13B 110.00
C14A—C4A—C3A 119.3 (2) H12B—C12B—H13B 108.00
C14A—C4A—C5A 119.6 (2) C13B—C12B—H12B 109.00

O1W—Mg1—O14A—C13A 56.7 (4) C2A—C3A—C4A—C5A −0.3 (4)
O3W—Mg1—O14A—C13A −126.6 (4) C3A—C4A—C5A—C6A 0.6 (5)
O4W—Mg1—O14A—C13A 144.3 (4) C4A—C4A—C5A—C6A 179.2 (2)
O5W—Mg1—O14A—C13A −37.1 (4) C4A—C5A—C6A—C1A −0.4 (4)
C12A—O11A—C1A—C2A 176.9 (3) O11A—C12A—C13A—O13A −5.8 (4)
C12A—O11A—C1A—C6A −3.6 (4) O11A—C12A—C13A—O14A 174.8 (2)

Acta Cryst. (2014). E70, 161-163 sup-5

electronic reprint
C1A—O11A—C12A—C13A 179.0 (2)
Mg1—O14A—C13A—O13A −60.7 (5)
Mg1—O14A—C13A—C12A 118.7 (3)
C12B—O11B—C1B—C2B −176.6 (3)
C12B—O11B—C1B—C6B 4.3 (4)
C6A—C1A—C2A—Cl2A −179.2 (2)
C1A—C2A—C3A—C4A −0.1 (5)

Hydrogen-bond geometry (Å, °)

| D—H···A       | D—H | H···A | D···A | D—H···A |
|---------------|------|-------|-------|---------|
| O1W—H11W···O13B | 0.86 (3) | 1.92 (3) | 2.772 (3) | 171 (3) |
| O1W—H12W···O4Wa | 0.87 (3) | 2.09 (3) | 2.939 (3) | 165 (3) |
| O2W—H21W···O14B | 0.88 (2) | 1.75 (2) | 2.623 (3) | 176 (3) |
| O2W—H22W···O14Bwa | 0.87 (3) | 1.88 (3) | 2.754 (3) | 173 (3) |
| O3W—H31W···O13Awi | 0.87 (2) | 1.80 (2) | 2.656 (3) | 167 (3) |
| O3W—H32W···C12Awi | 0.87 (3) | 2.50 (3) | 3.345 (2) | 165 (3) |
| O4W—H41W···O13A′ | 0.89 (2) | 1.77 (2) | 2.652 (3) | 172 (4) |
| O4W—H42W···O2Wa | 0.88 (2) | 2.19 (3) | 2.980 (3) | 151 (3) |
| O5W—H51W···O6W′ | 0.90 (5) | 1.90 (6) | 2.543 (5) | 127 (4) |
| O5W—H52W···O13Bwi | 0.88 (4) | 1.86 (4) | 2.708 (4) | 162 (4) |
| O6W—H61W···O14Bwi | 0.91 (6) | 1.77 (6) | 2.654 (5) | 162 (7) |
| O6W—H62W···O14A′ | 0.90 (6) | 2.12 (5) | 3.006 (5) | 168 (5) |

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