

Poly[hexaaquatri- μ -malonato-didysprosium(III)]

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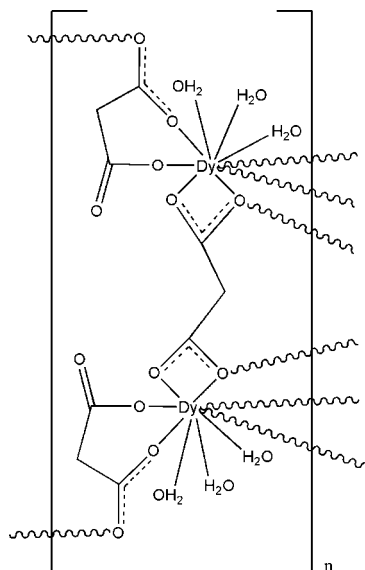
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.020; wR factor = 0.053; data-to-parameter ratio = 16.2.

The title compound, $[\text{Dy}_2(\text{C}_3\text{H}_2\text{O}_4)_3(\text{H}_2\text{O})_6]_n$, forms a coordination polymeric structure comprising hydrated dysprosium ions and malonate ligands. In the asymmetric unit, there are one dysprosium ion, one and a half malonate ligands, and three water molecules. Each Dy^{III} atom is coordinated by six O atoms from four malonate ligands and by three water molecules, and displays a tricapped trigonal-prismatic coordination geometry. The malonate ligands adopt two types of coordination mode, linking dysprosium centres to form a three-dimensional coordination polymer. The extensive network of hydrogen bonds in this polymer enhances the structural stability.

Related literature

For related literature, see: Iglesias *et al.* (2003); Kim *et al.* (2003); Moulton & Zaworotko (2001).



Experimental

Crystal data

$[\text{Dy}_2(\text{C}_3\text{H}_2\text{O}_4)_3(\text{H}_2\text{O})_6]$
 $M_r = 739.23$

Monoclinic, $C2/c$
 $a = 17.1805$ (2) Å
 $b = 12.3124$ (1) Å
 $c = 11.1541$ (1) Å
 $\beta = 127.52$ (2)°

$V = 1871.4$ (5) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 8.02$ mm⁻¹
 $T = 296$ (2) K
 $0.11 \times 0.10 \times 0.08$ mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2004)
 $T_{\text{min}} = 0.435$, $T_{\text{max}} = 0.529$

10051 measured reflections
2136 independent reflections
2001 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
 $wR(F^2) = 0.053$
 $S = 1.07$
2136 reflections
132 parameters

10 restraints
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.91$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1W}-\text{H1W}\cdots\text{O5}^{\text{i}}$	0.82	2.04	2.854 (4)	172
$\text{O1W}-\text{H2W}\cdots\text{O3}^{\text{ii}}$	0.81	1.94	2.729 (4)	165
$\text{O2W}-\text{H3W}\cdots\text{O3}^{\text{iii}}$	0.82	1.95	2.761 (4)	170
$\text{O3W}-\text{H6W}\cdots\text{O4}^{\text{iii}}$	0.81	2.02	2.802 (4)	160
$\text{O3W}-\text{H6W}\cdots\text{O3}^{\text{iii}}$	0.81	2.59	3.291 (4)	144
$\text{O3W}-\text{H5W}\cdots\text{O2}^{\text{iv}}$	0.81	1.96	2.738 (4)	161

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003) and *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2344).

References

- Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
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Kim, J. C., Jo, H., Lough, A. J., Cho, J., Lee, U. & Pyun, S. Y. (2003). *Inorg. Chem. Commun.* **6**, 474–477.
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supporting information

Acta Cryst. (2008). E64, m877 [doi:10.1107/S1600536808015961]

Poly[hexaaquatri- μ -malonato-didysprosium(III)]**Zhan-Qiang Fang, Rong-Hua Zeng, Zhao-Feng Song and Mei Yang****S1. Comment**

Molecular self-assembly of supramolecular architectures has received much attention during recent decades (Kim *et al.*, 2003; Iglesias *et al.*, 2003; Moulton & Zaworotko, 2001). The structures and properties of such systems depend on the coordination and geometric preferences of both the central metals ions and bridging building blocks as well as the influence of weaker non-covalent interactions, such as hydrogen bonds and π - π stacking interactions. Recently, we obtained the title compound, (I), by the hydrothermal reaction of $\text{Dy}(\text{NO}_3)_3$ with malonic acid in alkaline aqueous solution.

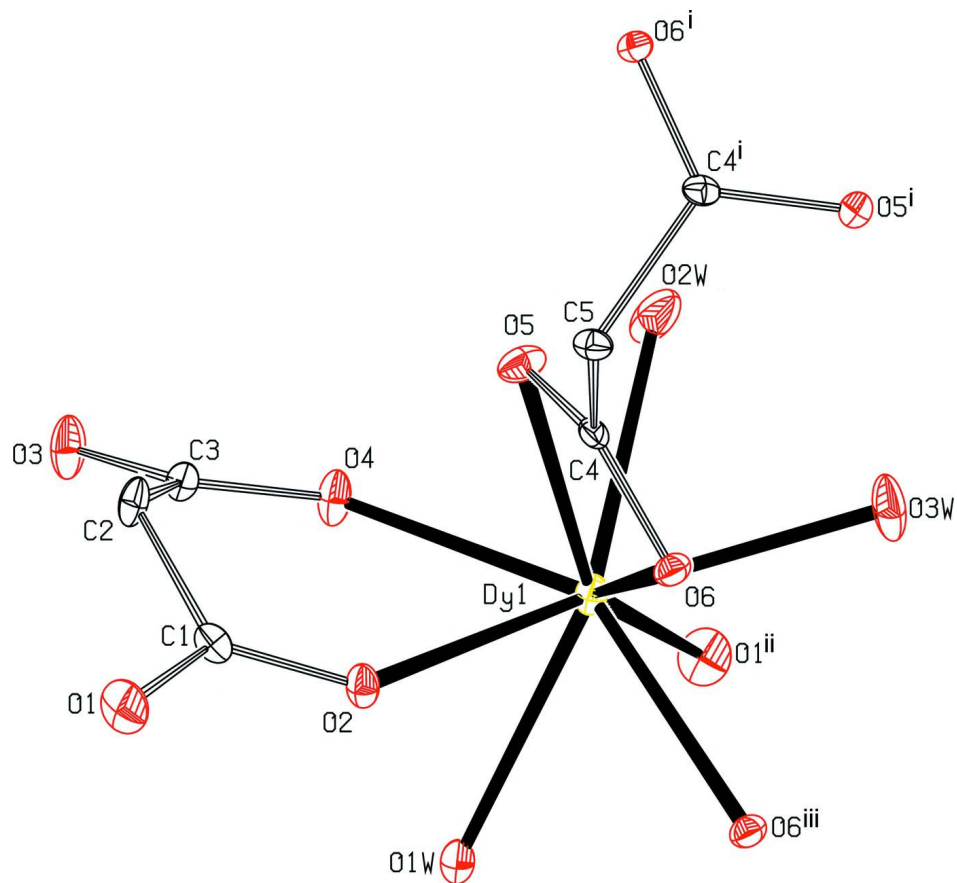
As illustrated in Fig. 1, in the asymmetric unit of complex (I), each Dy^{III} centre is coordinated by six carboxyl O atoms from four malonate ligands, and three water molecules. The two unique malonate ligands act as two types of chelating and bridging modes: one lies on an inversion centre and uses each carboxylate group to bond to two Dy^{III} ions; one uses three carboxyl O atoms to coordinate to two Dy^{III} ions involving a six-membered chelate ring. The adjacent $\text{Dy}\cdots\text{Dy}$ separations are 4.303 (3), 6.600 (1) and 6.982 (2) Å respectively. The ligands link dysprosium centres to form a three-dimensional coordination polymer which is also stabilized by the extensive network of hydrogen bonding interactions (Fig. 2; Table 1).

S2. Experimental

A mixture of $\text{Dy}(\text{NO}_3)_3$ (0.1 mmol), malonato acid (0.15 mmol), NaOH (0.1 mmol), water (10 ml) was stirred vigorously for 20 min and then sealed in a Teflon-lined stainless-steel autoclave (20 ml, capacity). The autoclave was heated to and maintained at 433 K for 7 days, and then cooled to room temperature at 5 K h^{-1} to obtain the colorless block crystals.

S3. Refinement

Water H atoms were tentatively located in difference Fourier maps and were refined with distance restraints of $\text{O}-\text{H} = 0.82$ Å and $\text{H}\cdots\text{H} = 1.30$ Å, and with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$, and then were treated as riding mode. Carbon-bound H atoms were placed at calculated positions and were treated as riding on the parent C atoms with $\text{C}-\text{H} = 0.97$ Å, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

**Figure 1**

The molecular structure showing the atomic-numbering scheme. Displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $1-x, y, 3/2-y$; (ii) $1/2-x, y-1/2, 1/2-z$; (iii) $1/2-x, 1/2-y, 1-z$]

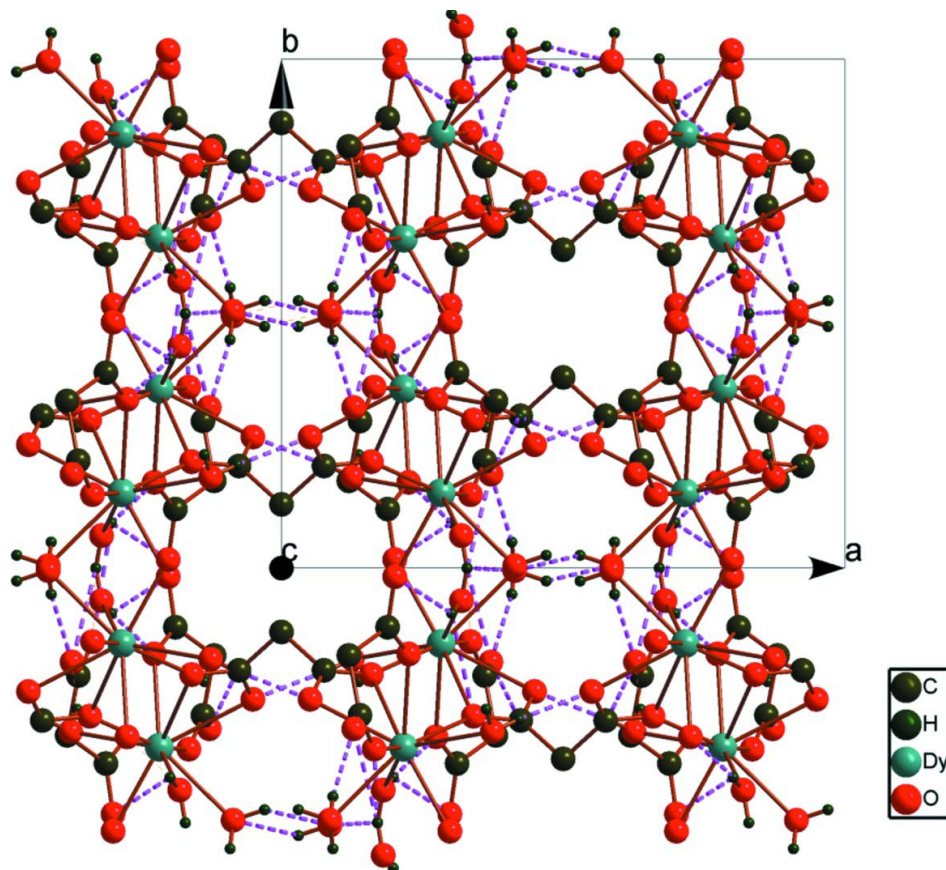
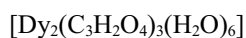


Figure 2

The molecular packing showing the intra/intermolecular hydrogen bonding interactions as broken lines.

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Crystal data



$M_r = 739.23$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 17.1805\ (2)\ \text{\AA}$

$b = 12.3124\ (1)\ \text{\AA}$

$c = 11.1541\ (1)\ \text{\AA}$

$\beta = 127.52\ (2)^\circ$

$V = 1871.4\ (5)\ \text{\AA}^3$

$Z = 4$

$F(000) = 1392$

$D_x = 2.624\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 6377 reflections

$\theta = 1.7\text{--}28.0^\circ$

$\mu = 8.02\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, colorless

$0.11 \times 0.10 \times 0.08\ \text{mm}$

Data collection

Bruker APEXII area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*APEX2*; Bruker, 2004)

$T_{\min} = 0.435$, $T_{\max} = 0.529$

10051 measured reflections

2136 independent reflections

2001 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -22 \rightarrow 20$

$k = -15 \rightarrow 15$

$l = -12 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.053$
 $S = 1.07$
 2136 reflections
 132 parameters
 10 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 12.727P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.91 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.3116 (3)	0.3839 (3)	0.2419 (4)	0.0139 (7)	
C2	0.3805 (3)	0.3285 (3)	0.2198 (5)	0.0174 (7)	
H2A	0.4462	0.3325	0.3148	0.021*	
H2B	0.3808	0.3704	0.1464	0.021*	
C3	0.3607 (3)	0.2110 (3)	0.1686 (4)	0.0137 (7)	
C4	0.4246 (2)	0.2993 (3)	0.6243 (4)	0.0119 (7)	
C5	0.5000	0.3747 (4)	0.7500	0.0135 (10)	
H5A	0.4703	0.4205	0.7829	0.016*	0.50
H5B	0.5297	0.4205	0.7171	0.016*	0.50
Dy1	0.283235 (12)	0.148077 (13)	0.379865 (19)	0.01461 (7)	
O1	0.2989 (2)	0.4832 (2)	0.2144 (4)	0.0268 (6)	
O2	0.2741 (2)	0.3315 (2)	0.2918 (3)	0.0165 (5)	
O3	0.3717 (2)	0.1844 (2)	0.0723 (3)	0.0256 (6)	
O4	0.3355 (2)	0.14437 (19)	0.2259 (3)	0.0200 (6)	
O5	0.44917 (18)	0.2424 (2)	0.5591 (3)	0.0192 (5)	
O6	0.34060 (17)	0.2909 (2)	0.5918 (3)	0.0144 (5)	
O1W	0.1257 (2)	0.1789 (2)	0.1179 (3)	0.0226 (6)	
H1W	0.0785	0.2029	0.1100	0.034*	
H2W	0.1369	0.2230	0.0756	0.034*	
O2W	0.4141 (3)	0.0048 (3)	0.4897 (5)	0.0435 (10)	
H3W	0.4088	-0.0512	0.5238	0.065*	
H4W	0.4700	0.0253	0.5538	0.065*	
O3W	0.3194 (2)	0.0640 (2)	0.6116 (4)	0.0322 (7)	
H6W	0.3294	-0.0003	0.6333	0.048*	
H5W	0.3019	0.0889	0.6593	0.048*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0179 (17)	0.0087 (15)	0.0121 (17)	0.0002 (13)	0.0077 (15)	-0.0012 (13)
C2	0.0267 (19)	0.0119 (16)	0.024 (2)	-0.0038 (14)	0.0211 (18)	-0.0010 (14)
C3	0.0166 (17)	0.0121 (16)	0.0163 (18)	-0.0007 (13)	0.0119 (15)	-0.0004 (13)
C4	0.0099 (15)	0.0139 (16)	0.0082 (16)	-0.0002 (12)	0.0037 (14)	0.0026 (13)
C5	0.010 (2)	0.011 (2)	0.014 (2)	0.000	0.005 (2)	0.000
Dy1	0.01901 (10)	0.01230 (10)	0.01759 (11)	-0.00036 (6)	0.01376 (8)	-0.00016 (6)
O1	0.0366 (17)	0.0102 (12)	0.0372 (18)	0.0042 (11)	0.0244 (15)	0.0062 (12)
O2	0.0249 (14)	0.0116 (12)	0.0203 (14)	0.0034 (10)	0.0175 (12)	0.0027 (10)
O3	0.0474 (18)	0.0187 (14)	0.0288 (16)	-0.0005 (13)	0.0326 (16)	-0.0014 (12)
O4	0.0366 (16)	0.0100 (12)	0.0276 (16)	-0.0013 (10)	0.0270 (14)	-0.0012 (10)
O5	0.0137 (12)	0.0264 (14)	0.0183 (13)	-0.0008 (10)	0.0102 (11)	-0.0068 (11)
O6	0.0104 (11)	0.0196 (13)	0.0131 (12)	-0.0015 (9)	0.0072 (10)	-0.0016 (10)
O1W	0.0206 (14)	0.0300 (15)	0.0198 (15)	-0.0003 (12)	0.0137 (12)	0.0065 (12)
O2W	0.0431 (19)	0.0277 (17)	0.085 (3)	0.0166 (15)	0.052 (2)	0.0281 (18)
O3W	0.063 (2)	0.0176 (14)	0.0415 (19)	0.0177 (14)	0.0450 (18)	0.0154 (13)

Geometric parameters (\AA , $^\circ$)

C1—O1	1.247 (4)	Dy1—O4	2.375 (3)
C1—O2	1.256 (4)	Dy1—O2	2.430 (2)
C1—C2	1.512 (5)	Dy1—O6 ⁱⁱⁱ	2.452 (2)
C2—C3	1.516 (5)	Dy1—O3W	2.487 (3)
C2—H2A	0.9700	Dy1—O2W	2.513 (3)
C2—H2B	0.9700	Dy1—O1W	2.524 (3)
C3—O3	1.243 (4)	Dy1—O5	2.555 (3)
C3—O4	1.266 (4)	Dy1—O6	2.610 (2)
C4—O5	1.254 (4)	O1W—H1W	0.8155
C4—O6	1.260 (4)	O1W—H2W	0.8146
C4—C5	1.514 (4)	O2W—H3W	0.8184
C5—C4 ⁱ	1.514 (4)	O2W—H4W	0.8133
C5—H5A	0.9700	O3W—H6W	0.8149
C5—H5B	0.9700	O3W—H5W	0.8144
Dy1—O1 ⁱⁱ	2.326 (3)		
O1—C1—O2	123.5 (3)	O4—Dy1—O1W	77.10 (10)
O1—C1—C2	116.0 (3)	O2—Dy1—O1W	68.42 (9)
O2—C1—C2	120.4 (3)	O6 ⁱⁱⁱ —Dy1—O1W	72.58 (9)
C1—C2—C3	118.3 (3)	O3W—Dy1—O1W	132.74 (10)
C1—C2—H2A	107.7	O2W—Dy1—O1W	132.85 (12)
C3—C2—H2A	107.7	O1 ⁱⁱ —Dy1—O5	146.20 (10)
C1—C2—H2B	107.7	O4—Dy1—O5	80.87 (9)
C3—C2—H2B	107.7	O2—Dy1—O5	70.15 (9)
H2A—C2—H2B	107.1	O6 ⁱⁱⁱ —Dy1—O5	113.70 (8)
O3—C3—O4	123.0 (3)	O3W—Dy1—O5	85.58 (10)
O3—C3—C2	117.3 (3)	O2W—Dy1—O5	72.37 (10)

O4—C3—C2	119.7 (3)	O1W—Dy1—O5	137.36 (9)
O5—C4—O6	121.2 (3)	O1 ⁱⁱ —Dy1—O6	141.99 (9)
O5—C4—C5	118.7 (3)	O4—Dy1—O6	124.57 (8)
O6—C4—C5	120.1 (3)	O2—Dy1—O6	68.62 (8)
C4—C5—C4 ⁱ	104.4 (4)	O6 ⁱⁱⁱ —Dy1—O6	63.60 (9)
C4—C5—H5A	110.9	O3W—Dy1—O6	67.78 (9)
C4 ⁱ —C5—H5A	110.9	O2W—Dy1—O6	107.42 (11)
C4—C5—H5B	110.9	O1W—Dy1—O6	119.61 (9)
C4 ⁱ —C5—H5B	110.9	O5—Dy1—O6	50.15 (8)
H5A—C5—H5B	108.9	C1—O1—Dy1 ^{iv}	159.0 (3)
O1 ⁱⁱ —Dy1—O4	92.80 (10)	C1—O2—Dy1	137.0 (2)
O1 ⁱⁱ —Dy1—O2	139.15 (10)	C3—O4—Dy1	138.4 (2)
O4—Dy1—O2	71.67 (8)	C4—O5—Dy1	95.7 (2)
O1 ⁱⁱ —Dy1—O6 ⁱⁱⁱ	89.46 (9)	C4—O6—Dy1 ⁱⁱⁱ	150.4 (2)
O4—Dy1—O6 ⁱⁱⁱ	147.09 (9)	C4—O6—Dy1	92.9 (2)
O2—Dy1—O6 ⁱⁱⁱ	85.38 (8)	Dy1 ⁱⁱⁱ —O6—Dy1	116.40 (9)
O1 ⁱⁱ —Dy1—O3W	78.76 (11)	Dy1—O1W—H1W	118.3
O4—Dy1—O3W	141.16 (9)	Dy1—O1W—H2W	107.9
O2—Dy1—O3W	136.14 (9)	H1W—O1W—H2W	105.4
O6 ⁱⁱⁱ —Dy1—O3W	71.36 (9)	Dy1—O2W—H3W	119.8
O1 ⁱⁱ —Dy1—O2W	73.98 (11)	Dy1—O2W—H4W	115.9
O4—Dy1—O2W	73.66 (10)	H3W—O2W—H4W	105.1
O2—Dy1—O2W	131.94 (9)	Dy1—O3W—H6W	126.0
O6 ⁱⁱⁱ —Dy1—O2W	137.86 (9)	Dy1—O3W—H5W	124.4
O3W—Dy1—O2W	67.55 (10)	H6W—O3W—H5W	105.5
O1 ⁱⁱ —Dy1—O1W	71.37 (10)		

Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $-x+1/2, y-1/2, -z+1/2$; (iii) $-x+1/2, -y+1/2, -z+1$; (iv) $-x+1/2, y+1/2, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1W \cdots O5 ^v	0.82	2.04	2.854 (4)	172
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O3W—H5W \cdots O2 ⁱⁱⁱ	0.81	1.96	2.738 (4)	161

Symmetry codes: (iii) $-x+1/2, -y+1/2, -z+1$; (v) $x-1/2, -y+1/2, z-1/2$; (vi) $-x+1/2, -y+1/2, -z$; (vii) $x, -y, z+1/2$.