

Tetra- μ -but-2-enoato-bis[di- μ -but-2-enoato]yttrium] di- μ -but-2-enoato-bis-[di- μ -but-2-enoato]yttrium] 4.6-hydrate

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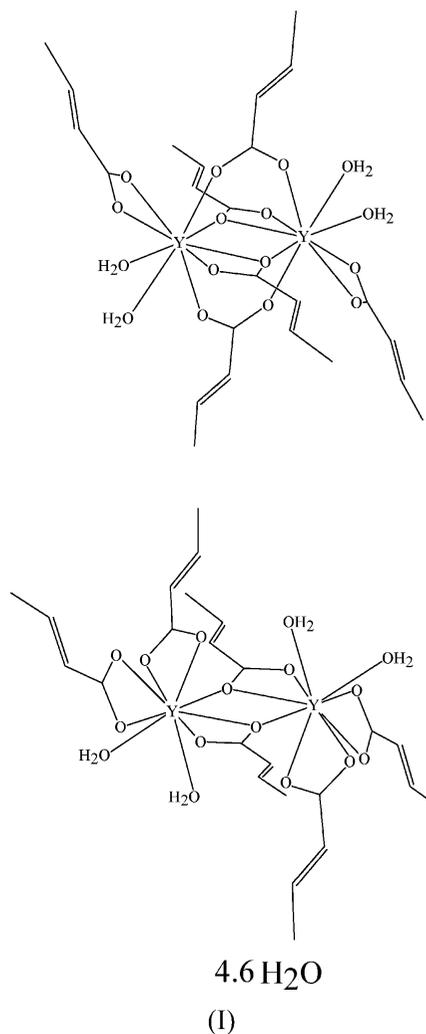
Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
H-atom completeness 99%
Disorder in main residue
 R factor = 0.043
 wR factor = 0.112
Data-to-parameter ratio = 17.6

The title compound, $[\text{Y}_2(\text{C}_4\text{H}_5\text{O}_2)_6(\text{H}_2\text{O})_4]_2 \cdot 4.6\text{H}_2\text{O}$, has two independent dimeric units, displaying different bridging patterns between metal ions which lead to dissimilar $\text{Y} \cdots \text{Y}$ distances. The compound is isostructural with an already reported Gd complex.

Comment

The title compound, (I) (Fig. 1), is isostructural with the Gd homolog described by Rizzi *et al.* (2003), where the reader is referred for additional details. It consists of two centrosymmetric dimers with the metal ions linked by different carboxylate bridging motifs, but with similar YO_9 cores (Fig. 2).



The Y1 dimer, quadruply bridged, shows $\text{Y1}-\text{O}$ distances spanning the range 2.285 (2)–2.571 (2) \AA (Table 1) with an

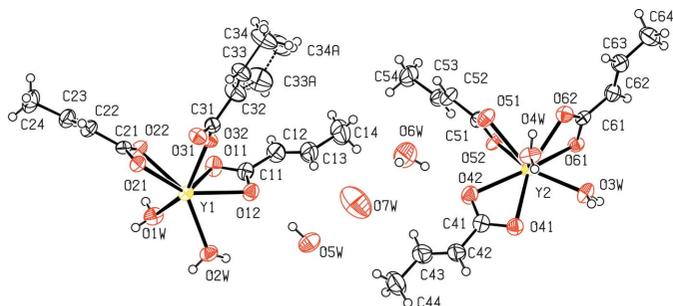


Figure 1

The structure of the asymmetric unit of (I) with the ellipsoids drawn at the 30% probability level and H atoms drawn as spheres of arbitrary radii. The disordered tail of one of the butenoate anions is shown as dashed lines.

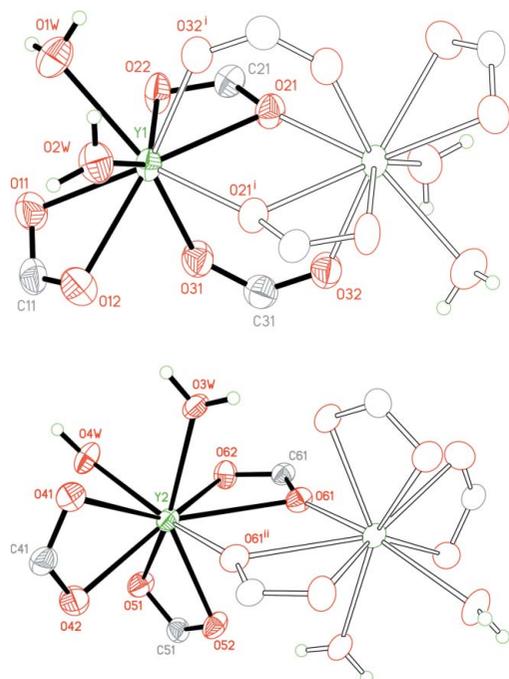


Figure 2

Coordination polyhedra for each independent dimer [top, Y1 dimer; bottom, Y2 dimer; symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $-x, -y, -z$], showing the differences in the inner dimer bridging modes. For clarity, only the carboxylate groups of the butenoate anions are shown.

average value of 2.406 (9) Å. The $Y1 \cdots Y1^i$ distance is 3.8789 (15) Å [symmetry code: (i) $1 - x, 2 - y, 1 - z$]. In the Y2 dimer, doubly bridged, the $Y2-O$ bond lengths span the range 2.314 (2)–2.631 (2) Å (Table 1) with a mean value of 2.412 (10) Å. The looser link between cations results in a longer $Y2 \cdots Y2^{ii}$ [symmetry code: (ii) $-x, -y, -z$] distance of 4.1123 (16) Å.

The shortest non-bridged metal \cdots metal distance between different dimers [$Y1 \cdots Y2^{iii}$, symmetry code: (iii): $x + 1, y + 1, z$] is 5.992 (1) Å. The two similar four-membered coordination loops in both polyhedra ($Y1-O21-Y1^i-O21^i$; $Y2-O61-Y2^{ii}-O61^{ii}$) are almost perpendicular to each other, their mean planes subtending a dihedral angle of 88.9 (1)°.

The dimers are linked together through a dense hydrogen-bonding network (Table 2) defining tight two-dimensional

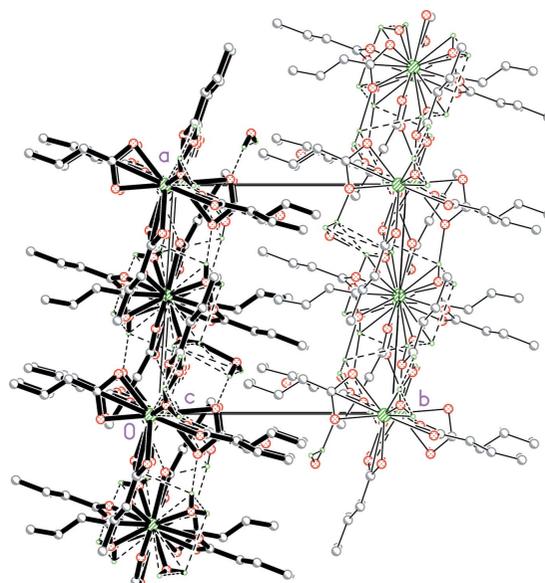


Figure 3

Packing view of (I) projected down the c axis, showing (sideways) two two-dimensional structures with interdigitated butenoate units in between.

structures parallel to (010), with metal atoms and hydrophilic parts at the centre, and the hydrophobic chains pointing outwards and interdigitating when these planes stack up along b (Fig. 3). Interplanar linkage is achieved through weak interactions involving disordered parts of the structure, *viz.* hydrogen bonds involving the partially occupied solvent water molecule O7W or the π - π contact between the centrosymmetrically related double bonds $C22=C23 \cdots C22^{vi}=C23^{vi}$ [symmetry code (vi): $1 - x, 1 - y, 1 - z$], with a mid-point-to-mid-point distance of 3.75 (1) Å.

Experimental

The complex was obtained by mixing a hot aqueous solution (30 ml) of crotonic acid (6 mmol) with an aqueous solution (20 ml) of Y_2O_3 (1 mmol). The resulting mixture was refluxed for 24 h, filtered while hot and then concentrated to 25 ml. The filtrate was left at room temperature. On standing, suitable crystals for single-crystal X-ray diffraction appeared and were used without further processing.

Crystal data

$[Y_2(C_4H_5O_2)_6(H_2O)_4]_2 \cdot 4.6H_2O$
 $M_r = 1603.60$
 Triclinic, $P\bar{1}$
 $a = 10.431$ (4) Å
 $b = 10.519$ (4) Å
 $c = 15.802$ (6) Å
 $\alpha = 89.382$ (6)°
 $\beta = 81.627$ (6)°
 $\gamma = 86.338$ (6)°

$V = 1711.9$ (11) Å³
 $Z = 1$
 $D_x = 1.556$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 3.45$ mm⁻¹
 $T = 298$ (2) K
 Block, colourless
 $0.22 \times 0.19 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)
 $T_{min} = 0.48, T_{max} = 0.56$

14298 measured reflections
 8173 independent reflections
 5632 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.035$
 $\theta_{max} = 27.9^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.112$
 $S = 0.97$
8173 reflections
465 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0649P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.65 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{Å}^{-3}$

Table 1

Selected bond lengths (Å).

| | | | |
|---------------------|-----------|----------------------|-----------|
| Y1—O21 ⁱ | 2.285 (2) | Y2—O61 ⁱⁱ | 2.314 (2) |
| Y1—O31 | 2.314 (2) | Y2—O4W | 2.322 (2) |
| Y1—O32 ⁱ | 2.332 (3) | Y2—O3W | 2.339 (2) |
| Y1—O2W | 2.390 (3) | Y2—O52 | 2.365 (2) |
| Y1—O11 | 2.415 (2) | Y2—O42 | 2.407 (3) |
| Y1—O1W | 2.444 (3) | Y2—O62 | 2.408 (3) |
| Y1—O12 | 2.451 (3) | Y2—O41 | 2.458 (2) |
| Y1—O22 | 2.452 (2) | Y2—O51 | 2.462 (3) |
| Y1—O21 | 2.571 (2) | Y2—O61 | 2.631 (2) |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--------------------------------------|----------|--------------|--------------|----------------|
| O1W—H1WA \cdots O41 ⁱⁱⁱ | 0.85 (3) | 1.88 (3) | 2.722 (4) | 171 (3) |
| O2W—H2WA \cdots O51 ^{iv} | 0.85 (2) | 1.90 (3) | 2.731 (4) | 164 (3) |
| O2W—H2WB \cdots O6W ^{iv} | 0.85 (2) | 2.09 (3) | 2.861 (6) | 151 (3) |
| O3W—H3WA \cdots O11 ^v | 0.85 (3) | 1.90 (3) | 2.738 (3) | 173 (4) |
| O3W—H3WB \cdots O52 ⁱⁱ | 0.85 (3) | 1.90 (3) | 2.703 (3) | 158 (3) |
| O4W—H4WA \cdots O22 ^v | 0.85 (3) | 1.90 (3) | 2.721 (3) | 164 (3) |
| O4W—H4WB \cdots O5W ^{vi} | 0.85 (3) | 2.05 (3) | 2.844 (4) | 158 (3) |
| O5W—H5WA \cdots O62 ^{iv} | 0.85 (2) | 2.10 (3) | 2.820 (4) | 141 (2) |
| O5W—H5WB \cdots O12 | 0.85 (2) | 2.06 (3) | 2.891 (4) | 165 (4) |
| O6W—H6WA \cdots O42 | 0.85 (3) | 2.03 (3) | 2.880 (5) | 176 (6) |
| O6W—H6WB \cdots O7W | 0.85 (3) | 2.22 (5) | 2.800 (16) | 126 (6) |

Symmetry codes: (ii) $-x, -y, -z$; (iii) $x + 1, y + 1, z$; (iv) $x, y + 1, z$; (v) $x - 1, y - 1, z$; (vi) $x, y - 1, z$.

H atoms attached to carbon were placed at idealized positions [C—H = 0.96 (CH₃) and 0.93 Å (CH)] and allowed to ride. Those of water molecules (except for the partially occupied O7W) were found in difference maps and refined with restrained O—H distances [0.85 (2) Å]. All H atoms were assigned an isotropic displacement parameter $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{parent atom})$, with $x = 1.5$ for methyl groups and $x = 1.2$ otherwise. One of the solvent water sites (O7W) appeared as partially occupied, and its site occupancy factor, initially refined, was finally fixed at 0.30; the isostructural Gd compound does not have this third solvent water molecule, probably because lower data quality impairs resolution. Atoms C33 and C34 of one of the butenoate units attached to Y1 are disordered over two sites with occupancy factors of 0.75/0.25. Their occupancy factors were allowed to vary in the early stages of refinement, and were fixed in the final stages at their convergence values of 0.75/0.25.

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2001); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2001); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

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