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The α polymorph of racemic tris(2,4-pentanedionato-κ^2O,O')vanadium(III), redetermined at 120 K

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Key indicators

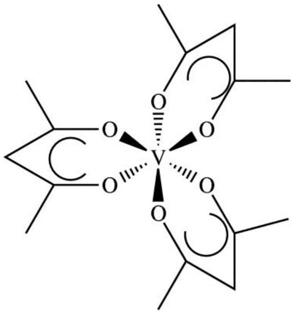
Single-crystal X-ray study
T = 120 K
Mean σ(Wae) = 0.000 Å
R factor = 0.058
wR factor = 0.135
Data-to-parameter ratio = 18.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the α polymorph of the title compound, $[V(C_5H_7O_2)_3]$, the molecules lie in general positions with no crystallographically imposed symmetry, but with approximate D_3 (32) molecular symmetry.

Comment

The title compound, (I) (Fig. 1), crystallizes in two structurally characterized polymorphs, an orthorhombic form in space group *Pbca*, denoted α, and a monoclinic form in space group $P2_1/n$, denoted β (Morosin & Montgomery, 1969). The orthorhombic α form has been structurally characterized only at ambient temperature (Morosin & Montgomery, 1969; Filgueiras *et al.*, 2001), but neither report mentioned the molecular stereochemistry. We have now taken the opportunity to redetermine the structure of this phase using diffraction data collected at 120 K: the unit-cell dimensions and space group confirm that the same phase is present at 120 K as at ambient temperature.



(I)

In the α polymorph of compound (I) the molecules lie in general positions in space group *Pbca*, but the local molecular symmetry is very close to the ideal D_3 (32) expected for isolated molecules. Although the compound is racemic, the molecules are chiral, but the centrosymmetric space group accommodates equal numbers of the Λ and Δ enantiomorphs: the selected reference molecule (Fig. 1) has Λ configuration. The corresponding bond distances within the three independent ligands show some modest variation, as exemplified by the V—O and O—C distances (Table 1); likewise the ligand bite angles O—V—O within the rings show minor variation. While two of the three rings are effectively planar, that including atoms O11 and O13 shows a minor puckering, and this ring is best described as forming a boat conformer with a total puckering amplitude of 0.199 (2) Å, with the maximum displacement from the mean ring plane found for the V atom of 0.138 (2) Å.

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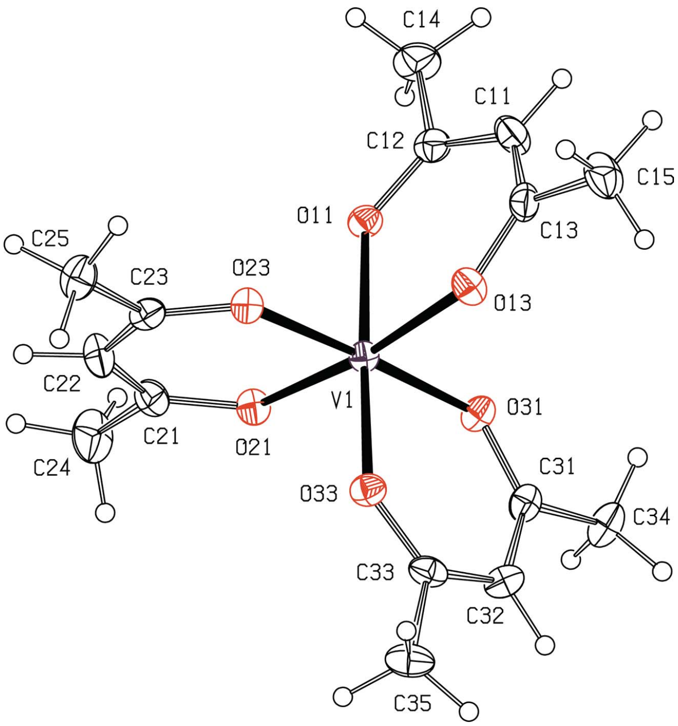

Figure 1
The Λ enantiomorph of compound (I) in the α polymorph, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Within each domain $0 < x < 0.5$ and $0.5 < x < 1.0$ there are four molecules, two of each enantiomer, with the Λ and Δ forms alternating, in chess-board fashion, on an approximately square grid (Fig. 2).

Experimental

The title compound was prepared from $VO(CH_3COCHCOCH_3)_2$, according to the published procedure of Grdenić & Korpar-Čolig (1964), except that powdered tin was employed as the reducing agent rather than powdered zinc [m.p. 457 K; literature m.p. (Grdenić & Korpar-Čolig, 1964) 457 K].

Crystal data

$[V(C_5H_7O_2)_3]$
$M_r = 348.26$
Orthorhombic, *Pbca*
$a = 13.3920\ (7)$ Å
$b = 16.4043\ (6)$ Å
$c = 15.1901\ (10)$ Å
$V = 3337.1\ (3)$ Å^3
$Z = 8$
$D_x = 1.386$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 3824 reflections
$\theta = 3.2$–$27.5°$
$\mu = 0.62$ mm^{-1}
$T = 120\ (2)$ K
Plate, brown
0.22 × 0.18 × 0.03 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.859$, $T_{\max} = 0.982$
30601 measured reflections
3824 independent reflections
1876 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.174$
$\theta_{\max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -21 \rightarrow 21$
$l = -19 \rightarrow 18$

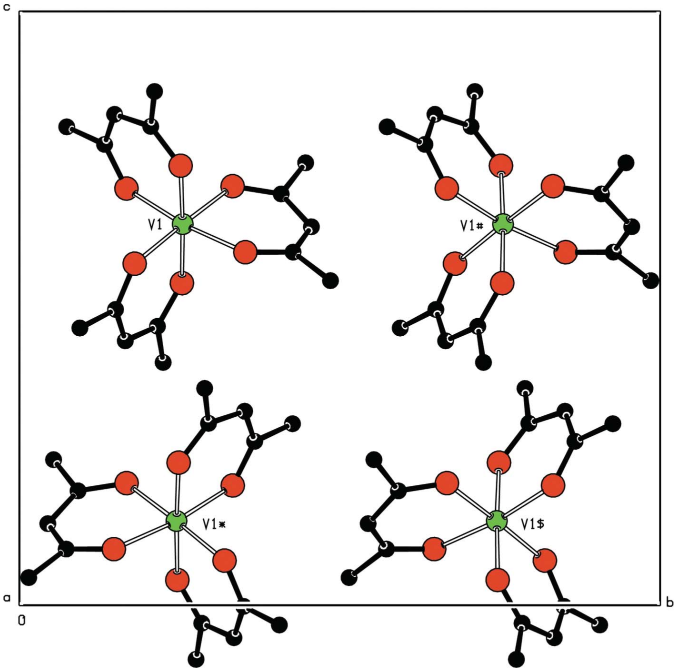

Figure 2
Projection on to (100) of the domain $0 < x < 0.5$ in the α polymorph of compound (I), showing the alternation of Λ and Δ enantiomorphs. For the sake of clarity, the H atoms have been omitted. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$, $(\frac{1}{2} - x, \frac{1}{2} + y, z)$ and $(\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z)$, respectively.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.135$
$S = 1.00$
3824 reflections
205 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.2837P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V1—O11	1.998 (2)	C11—O11	1.272 (4)
V1—O13	1.983 (2)	C13—O13	1.279 (4)
V1—O21	1.971 (2)	C21—O21	1.283 (4)
V1—O23	2.006 (2)	C23—O23	1.263 (4)
V1—O31	1.986 (2)	C31—O31	1.271 (4)
V1—O33	1.959 (2)	C33—O33	1.284 (4)
O11—V1—O13	86.30 (10)	O31—V1—O33	88.74 (9)
O21—V1—O23	88.35 (9)		

All H atoms were located in difference maps, and then treated as riding atoms, with C—H distances 0.95 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$ for the ring CH atoms, and C—H distances 0.98 Å and $U_{\rm iso}(H) = 1.5U_{\rm eq}(C)$ for the methyl groups.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England. The authors thank the staff for all their help and advice.

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