

α -Form of tris(2,4-pentanedionato-*O,O'*)vanadium(III), re-refinement against new intensity data

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Key indicators

Single-crystal X-ray study

$T = 297\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.044

w R factor = 0.139

Data-to-parameter ratio = 25.1

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

The title compound, $\text{V}(\text{MeCOCHCOMe})_3$ or $[\text{V}(\text{C}_5\text{H}_7\text{O}_2)_3]$, has been prepared by an unusual route. Its structure, confirming its identity, is the same as that reported by Morosin & Montgomery [*Acta Cryst.* (1969), B25, 1354–1359] but enhanced in precision.

Comment

There are at least two previous reports of the preparation of the title compound, (I), which is also known as tris(acetylacetonato)vanadium(III). Grdenic & Korper-Colig (1964) prepared it by reaction of $\text{VO}(\text{acac})_2$ with Zn and 2,4-pentanedione (Hacac). It has also been obtained (Morosin & Montgomery, 1969) by the reaction of $\text{V}_2(\text{SO}_4)_3$ (obtained by the electrolytic reduction of VOSO_4) with Hacac in sodium carbonate solution. Morosin & Montgomery described two crystalline forms of the material, a monoclinic β form [refcode in Cambridge Structural Database (Allen & Kennard, 1993): VAACAC01], and the orthorhombic α form (VAACAC) whose structure was determined and refined on the basis of 3061 reflections with 1361 classed as observed [$I > 3\sigma(I)$]. The improved precision of the re-refinement of the α form (I) presented here is attributed to a more extensive and better quality set of intensity data (see Tables) in conjunction with the use of up-to-date software (*SHELXL97*; Sheldrick, 1997).

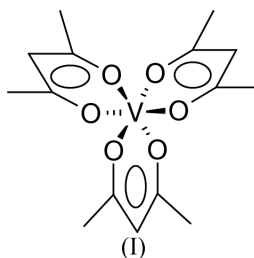


Fig. 1 shows the molecule and atom labelling scheme [identical to that used by Morosin & Montgomery (1969)] and Table 1 compares selected bond distances and angles between their determination and this work.

Experimental

Compound (I) was obtained from $\text{VO}(\text{acac})_2$ (0.400 g, 1.50 mmol) and a slight excess (*ca.* 1.75 mmol) of $\text{K}[\text{SnPh}_3]$ prepared from Ph_3SnH and KH , in tetrahydrofuran solution under an argon atmosphere. The deep-purple solution was stirred at room temperature for 1 h, concentrated, hexane added, and the mixture left in a freezer for 3 d. After filtering off an amorphous brown precipitate, the solution was left for a further period after which dark-orange brown crystals of (I) were deposited and collected [m.p. 460–461 K; literature 459–462 K (Morosin & Montgomery, 1969)].

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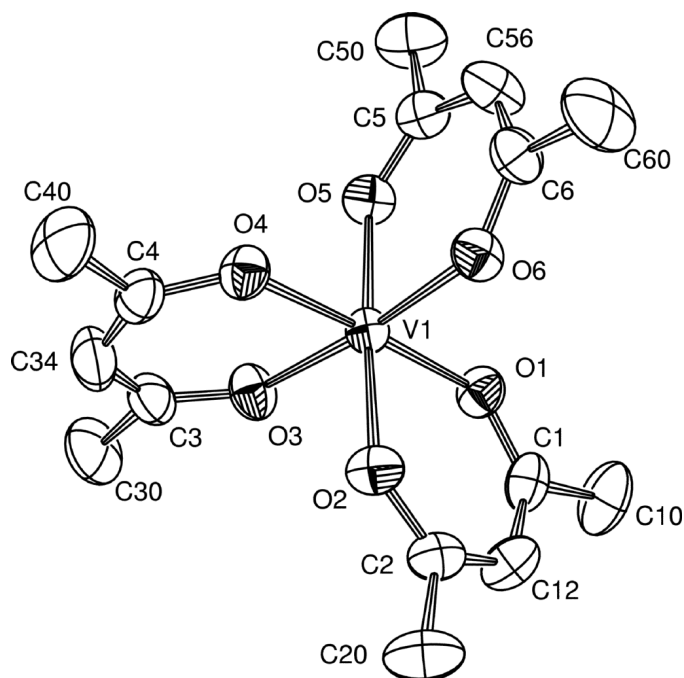


Figure 1
The molecule of (I) showing the labelling scheme. Non-H atoms are shown as 50% probability ellipsoids. H atoms have been omitted for clarity.

Crystal data

$[\text{V}(\text{C}_5\text{H}_7\text{O}_2)_3]$

$M_r = 348.26$

Orthorhombic, $Pcab$

$a = 15.4466$ (7) Å

$b = 16.6228$ (8) Å

$c = 13.5016$ (6) Å

$V = 3466.7$ (3) Å³

$Z = 8$

$D_x = 1.334$ Mg m⁻³

$D_m = 1.33$ Mg m⁻³

D_m measured by flotation in CCl_4/EtOH (Morosin & Montgomery, 1969)

Mo $K\alpha$ radiation

Cell parameters from 4494 reflections

$\theta = 2.4\text{--}26.4^\circ$

$\mu = 0.60$ mm⁻¹

$T = 297$ (2) K

Block, dark orange–brown

$0.30 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART 1000 area-detector diffractometer

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1999)

$T_{\min} = 0.445$, $T_{\max} = 0.928$

28 129 measured reflections

5155 independent reflections

2251 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\text{max}} = 31.0^\circ$

$h = -22 \rightarrow 14$

$k = -23 \rightarrow 24$

$l = -17 \rightarrow 18$

Intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.139$

$S = 0.94$

5155 reflections

205 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.003$

$\Delta\rho_{\text{max}} = 0.29$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.56$ e Å⁻³

Table 1

Comparison table of selected bond distances (Å) and angles (°).

	VAACAC		This work	
	min.	max.	min.	max.
V—O	1.967 (8)	1.995 (8)	1.9688 (17)	1.9912 (18)
C—O	1.235 (14)	1.268 (14)	1.257 (3)	1.268 (3)
endo-C—C	1.376 (19)	1.408 (19)	1.363 (4)	1.390 (4)
C—Me	1.497 (21)	1.528 (21)	1.497 (4)	1.516 (3)
Ligand bite	87.5 (6)	88.4 (6)	87.23 (8)	88.18 (7)

Refinement was started on the basis of coordinates for non-H atoms extracted from the Cambridge Structural Database (Allen & Kennard, 1993) (VAACAC; Morosin & Montgomery, 1969) by means of the EPSRC's chemical database service at Daresbury (Fletcher *et al.*, 1996). The non-standard space group setting and atom labels of the original determination were retained, but the cell dimensions were adjusted appropriately for the new intensity data. In the final stages, H atoms were placed in calculated positions (C—H = 0.96 and 0.93 Å for methyl and alkene H atoms, respectively) and refined in a riding-model approximation. Methyl groups were treated as rigid bodies. The incompleteness (92.95% complete) of the intensity data available for this re-refinement is due to the presence of a few defective frames in the raw intensity data.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

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