

## Racemic *cis*-methoxobis(2-methyl-3-oxo-4*H*-pyran-4-olato)oxovanadium(V) redetermined at 120 K: hydrogen-bonded ribbons containing $R_2^2(7)$ , $R_2^2(14)$ and $R_4^4(18)$ rings

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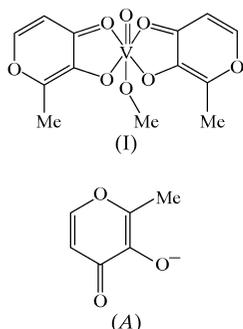
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In the title compound,  $[\text{V}(\text{CH}_3\text{O})(\text{C}_6\text{H}_5\text{O}_3)_2\text{O}]$ , the V—O bond lengths to the oxo and methoxo ligands are 1.593 (3) and 1.768 (3) Å, respectively, at 120 K; the V—O bond lengths *trans* to these two ligands are 2.246 (3) and 2.116 (3) Å. Molecules are linked by three C—H···O hydrogen bonds into complex ribbons containing three types of ring.

### Comment

3-Hydroxy-2-methyl-4-pyrone (maltol) is both a food additive (E636) and a versatile ligand for the design of insulin-enhancing vanadium complexes, and several vanadium complexes of maltol derivatives have been shown to be active insulin enhancers (McNeill *et al.*, 1992; Thompson *et al.*, 2003; Saatchi *et al.*, 2005). The reaction between maltol and tris(pentane-2,4-dionato)vanadium(III) was studied in the hope of producing a mixed-ligand complex of vanadium(III)

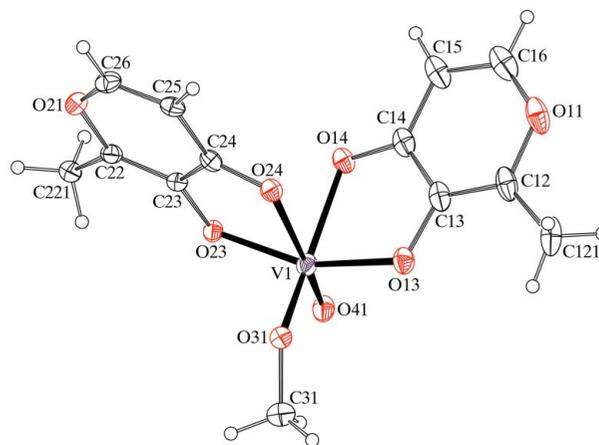


containing both maltolate and pentane-2,4-dionate ligands; in the event, the crystalline product isolated is the title

compound, (I) (Fig. 1), a complex of vanadium(V) containing no pentane-2,4-dionate ligands.

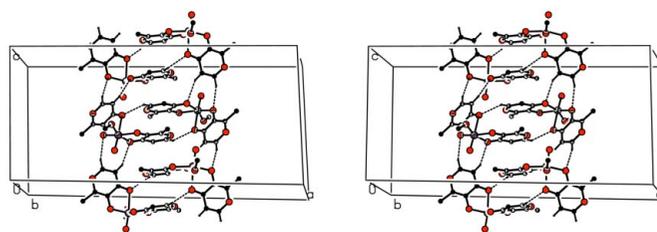
The structure of (I) has been reported previously from diffraction data collected at ambient temperature (Sun *et al.*, 1996); in that study, the compound had been formed as the product of aerial oxidation of bis(2-methyl-3-oxo-4-pyrone-3-olato)oxovanadium(IV) in methanol solution. The ready formation of (I) from both vanadium(III) and vanadium(IV) precursors indicates its high thermodynamic stability. This earlier structure determination (Sun *et al.*, 1996) was intended as a proof of composition and constitution, and no mention whatever was made of any intermolecular interactions. We have now taken the opportunity to redetermine this structure using diffraction data collected at 120 K, and we also present a full description of the supramolecular aggregation. The unit-cell dimensions and the space group indicate that no phase change has occurred between ambient temperature and 120 K.

Apart from the oxo and methoxo substituents, the remainder of the complex has approximately twofold rotational symmetry, but overall there is no even approximate internal symmetry. Accordingly, the molecules are chiral, although the compound is racemic. The centrosymmetric space group accommodates equal numbers of  $\Lambda$  and  $\Delta$  enantiomers; the selected reference molecule has the  $\Lambda$  configuration. The intermolecular geometry found at 120 K



**Figure 1**

The  $\Lambda$  enantiomer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.



**Figure 2**

A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded ribbon along [001]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

closely resembles that reported at ambient temperature. The bond distances (Table 1) for the pyran ligands support the bond-fixed form (A) (see scheme), although the C14—O14 and C24—O24 bonds are long for their type (Allen *et al.*, 1987). However, the differences between the C16—O11 and C26—O21 bond distances on the one hand, and C12—O11 and C22—O21 on the other, which are also apparent in the ambient-temperature structure although not remarked upon (Sun *et al.*, 1996), have no obvious simple explanation.

The molecules of (I) are linked into a rather complex ribbon by three independent C—H...O hydrogen bonds (Table 2) in which the acceptors are three of the four O atoms in the chelate rings; surprisingly, oxo ligand O41 is not involved in the hydrogen bonding. The formation of the chain is readily analysed in terms of two simple substructures. In the first substructure, atom C16 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom O24 in the molecule at (1 - *x*, 1 - *y*, 1 - *z*), so forming a cyclic centrosymmetric  $R_2^2(14)$  (Bernstein *et al.*, 1995) dimer (Fig. 2), which contains one  $\Delta$  molecule and one  $\Delta$  molecule and so is itself achiral.

In the second substructure, atoms C25 and C26 in the molecule at (*x*, *y*, *z*) act as hydrogen-bond donors, respectively, to atoms O14 and O23, both in the molecule at (*x*, 1 - *y*,  $\frac{1}{2} + z$ ), so forming a  $C(6)C(6)[R_2^2(7)]$  chain of rings running parallel to the [001] direction and generated by the *c*-glide plane at  $y = \frac{1}{2}$  (Fig. 2). The combination of these two motifs then generates a ribbon along [001]; in the central strip of this ribbon, there are  $R_2^2(14)$  rings centred at  $[\frac{1}{2}, \frac{1}{2}, (n + 1)/2]$  (*n* = zero or integer) alternating with  $R_4^4(18)$  rings, and this chain of edge-fused rings is flanked by two antiparallel arrays of  $R_2^2(7)$  rings (Fig. 2). Two such ribbons, related to one another by the *C*-centring operation, pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

## Experimental

A mixture of tris(pentane-2,4-dionato)vanadium(III) (0.30 g) and 3-hydroxy-2-methyl-4-pyrone (0.19 g) in methanol (30 ml) was heated under reflux for 3 h under an atmosphere of dinitrogen. The resulting solution was cooled and then concentrated under reduced pressure to provide crystals of (I) suitable for single-crystal X-ray diffraction (no melting point, decomposition above 570 K).

### Crystal data

[V(CH <sub>3</sub> O)(C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>2</sub> O]	$D_x = 1.623 \text{ Mg m}^{-3}$
$M_r = 348.17$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3249 reflections
$a = 28.007(2) \text{ \AA}$	$\theta = 3.1\text{--}27.5^\circ$
$b = 7.6637(6) \text{ \AA}$	$\mu = 0.74 \text{ mm}^{-1}$
$c = 13.3083(10) \text{ \AA}$	$T = 120(2) \text{ K}$
$\beta = 93.937(4)^\circ$	Plate, red
$V = 2849.7(4) \text{ \AA}^3$	$0.10 \times 0.03 \times 0.01 \text{ mm}$
$Z = 8$	

### Data collection

Nonius KappaCCD diffractometer	1976 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.092$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.954$ , $T_{\text{max}} = 0.993$	$h = -36 \rightarrow 29$
10000 measured reflections	$k = -9 \rightarrow 8$
3249 independent reflections	$l = -17 \rightarrow 17$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 6.4183P]$
$R[F^2 > 2\sigma(F^2)] = 0.069$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.158$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
3249 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$
202 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

V1—O13	1.947 (3)	V1—O23	1.915 (3)
V1—O14	2.116 (3)	V1—O24	2.246 (3)
V1—O31	1.768 (3)	V1—O41	1.593 (3)
C13—O13	1.347 (5)	C23—O23	1.342 (5)
C14—O14	1.265 (5)	C24—O24	1.263 (5)
C12—C13	1.360 (6)	C22—C23	1.354 (6)
C13—C14	1.425 (7)	C23—C24	1.433 (5)
C14—C15	1.425 (7)	C24—C25	1.432 (6)
C15—C16	1.357 (7)	C25—C26	1.331 (6)
O11—C12	1.375 (6)	O21—C22	1.370 (5)
O11—C16	1.331 (7)	O21—C26	1.339 (5)
O13—V1—O14	78.67 (12)	O23—V1—O24	77.88 (11)

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C16—H16...O24 <sup>i</sup>	0.95	2.42	3.174 (6)	136
C25—H25...O14 <sup>ii</sup>	0.95	2.48	3.331 (5)	149
C26—H26...O23 <sup>ii</sup>	0.95	2.44	3.351 (5)	161

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

The systematic absences permitted *Cc* and *C2/c* as possible space groups; *C2/c* was selected and confirmed by the subsequent structure analysis. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (ring H atoms) or 0.98  $\text{\AA}$  (methyl H atoms), and with  $U_{\text{iso}}(\text{H})$  values of 1.2 $U_{\text{eq}}(\text{C})$  or 1.5 $U_{\text{eq}}(\text{methyl C})$ .

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.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1897). Services for accessing these data are described at the back of the journal.

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