C7	−0.0604 (4)	0.7978 (4)	0.1516 (1)	2.5 (1)
C8	0.0335 (5)	0.8270 (5)	0.1717 (1)	2.9 (1)
C9	0.0269 (5)	0.9347 (5)	0.1785 (1)	2.8 (1)
C10	−0.0729 (4)	0.9717 (4)	0.1628 (1)	2.2 (1)
C11	0.2714 (4)	1.0616 (4)	0.1833 (1)	2.6 (1)
C12	0.1888 (5)	1.1419 (4)	0.1765 (2)	2.8 (1)
C13	0.1465 (5)	1.1297 (4)	0.1422 (1)	2.6 (1)
C14	0.1975 (4)	1.0385 (4)	0.1260 (1)	2.2 (1)
C15	0.2770 (4)	1.0021 (5)	0.1524 (1)	2.6 (1)
C16	0.2944 (5)	0.8883 (5)	−0.0130 (2)	3.8 (1)
C17	0.2107 (6)	1.0863 (5)	0.0226 (2)	3.9 (2)
C18	0.4110 (5)	0.9657 (5)	0.0539 (2)	4.1 (1)
C19	−0.3281 (5)	1.0219 (5)	0.1257 (2)	3.9 (1)
C20	−0.3597 (6)	0.7999 (6)	0.1547 (2)	5.4 (2)
C21	−0.2728 (5)	0.8313 (5)	0.0792 (2)	4.0 (1)
C22	0.298 (1)	0.914 (1)	0.2453 (4)	6.1 (4)
C22′	0.425 (1)	1.140 (1)	0.2437 (4)	5.9 (4)
C23	0.310 (2)	1.147 (1)	0.2574 (4)	7.7 (5)
C23′	0.433 (2)	0.915 (1)	0.2218 (5)	9.2 (5)
C24	0.500 (1)	1.037 (3)	0.2175 (5)	15.4 (9)
C24′	0.230 (2)	0.998 (3)	0.2621 (5)	15.1 (9)

Table 2. *Selected geometric parameters* (Å, °)

*Cp*1 and *Cp*2 are the centroids of the η^5-cyclopentadienyl rings.

Zr—Cl	2.442 (1)	Zr—C14	2.396 (5)
Zr—*Cp*1	2.227	Zr—*Cp*2	2.200
Zr—C1	2.591 (5)	Zr—C6	2.536 (5)
Zr—C2	2.519 (5)	Zr—C7	2.501 (5)
Zr—C3	2.488 (6)	Zr—C8	2.500 (5)
Zr—C4	2.491 (6)	Zr—C9	2.500 (5)
Zr—C5	2.553 (5)	Zr—C10	2.509 (5)
C11—C12	1.447 (8)	C11—C15	1.381 (8)
C12—C13	1.383 (8)	C13—C14	1.447 (8)
C14—C15	1.446 (8)		
*Cp*1—Zr—*Cp*2	127.8	Cl—Zr—C14	92.1 (1)

The structure was solved partially by direct methods (*SHELXS*86; Sheldrick, 1985), the remaining atoms being located by Fourier methods. C atoms of the trimethylsilyl group on the η^1-cyclopentadienyl ring (C22, C23 and C24) had large displacement parameters and excess electron density between them indicating disorder which was modeled by two sets of methyl C atoms (occupancy 0.5) related by a rotation of 180° about the Si3—C11 axis. Residual electron density in the final Fourier synthesis is associated with this trimethylsilyl group. All non-H atoms were refined with anisotropic displacement parameters. Each H atom was placed in a calculated position with a fixed displacement parameter of 1.3 times that of the C atom to which it is attached. The structure refinement used *MolEN* (Fair, 1990) and local unpublished programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: MU1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Oxobis(2,4-pentanedionato)vanadium(IV), a Redetermination

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Abstract

A redetermination of oxobis(2,4-pentanedionato)vanadium(IV), $[VO(C_5H_7O_2)_2]$, has been undertaken using high-resolution Mo data. Geometrical parameters do not differ significantly from those reported earlier [Dodge, Templeton & Zalkin (1961). *J. Chem. Phys.* **35**, 55–67; Hon, Belford & Pfluger (1965). *J. Chem. Phys.* **43**, 3111–3115], but the standard deviations are improved by an order of magnitude. Important structural parameters: V—O(basal) 1.967 (1)–1.970 (1) Å and V=O(apical) 1.584 (2) Å.

Comment

Current interest in orally active insulin mimics, particularly vanadium compounds (Shechter, 1990; Shechter *et al.*, 1990), has prompted a redetermination of the structure of oxobis(2,4-pentanedionato)vanadium(IV), (I). Since some of the promising vanadium-containing insulin mimics are structurally related to vanadyl bis(β-

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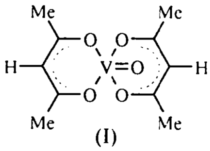
diketonate) species (McNeill, Yuen, Hoveyda & Orvig, 1992, and references therein), an accurate structure of one of the simplest members of this class of compounds would facilitate the assessment of structural subtleties which may be an important factor in determining the potency of the insulin-mimicking effect.



(I)

The original report of the structure (Dodge, Templeton & Zalkin, 1961) is based on a visual Cu data set. A later paper reports an anisotropic refinement using the same set of data (Hon, Belford & Pfluger, 1965). Bond lengths and angles do not differ significantly from those reported earlier. However, the C_5O_2 groups of the 2,4-pentanedionate ligands now exhibit significant deviations from planarity [maximum deviations: C(5) 0.073 (3) and C(10) 0.136 (3) Å]. The V atom is displaced 0.5447 (4) Å from the mean plane of the basal O atoms, and 0.2600 (4) and 0.3594 (4) Å from the seven-atom ligand mean planes defined by O(1), O(2), C(1)–C(5) and O(3), O(4), C(6)–C(10), respectively. The angle between the normals to the two ligand mean planes is 159.6°.

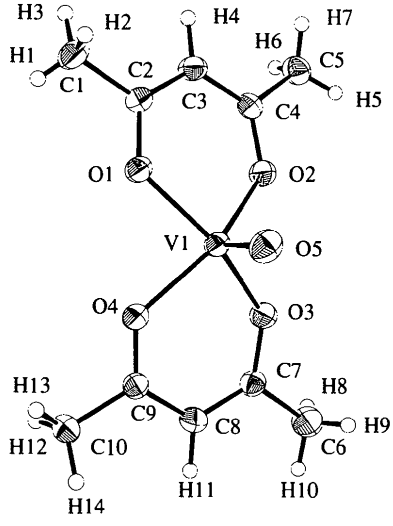


Fig. 1. Perspective view of the molecule with 33% displacement ellipsoids shown for the non-H atoms.

Experimental

Crystal data

$[VO(C_5H_7O_2)_2]$
$M_r = 265.16$
Triclinic
$P\bar{1}$
$a = 8.2116$ (7) Å
$b = 11.229$ (1) Å
$c = 7.5178$ (9) Å
$\alpha = 108.507$ (8)°
$\beta = 113.336$ (7)°
$\gamma = 73.187$ (7)°
$V = 592.9$ (1) Å^3
$Z = 2$
$D_x = 1.485$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 15.5$–16.9°
$\mu = 0.810$ mm^{-1}
$T = 294$ K
Plate
0.35 × 0.25 × 0.10 mm
Green
Crystal source: material from Aldrich Chemical recrystallized from methanol

Data collection

AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: empirical (ψ scans for three reflections)
$T_{min} = 0.947$, $T_{max} = 1.000$
6559 measured reflections
6223 independent reflections
2760 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.025$
$\theta_{max} = 37.5°$
$h = 0 \rightarrow 14$
$k = -17 \rightarrow 19$
$l = -12 \rightarrow 11$
3 standard reflections monitored every 200 reflections
intensity variation: 2.3%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.035$
$S = 1.87$
2760 reflections
201 parameters
All H-atom parameters refined

Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
V(1)	0.29030 (5)	0.22315 (3)	0.35637 (5)	0.03519 (9)
O(1)	0.2298 (2)	0.0525 (1)	0.2778 (2)	0.0412 (4)
O(2)	0.5343 (2)	0.1371 (1)	0.3499 (2)	0.0412 (4)
O(3)	0.4157 (2)	0.3583 (1)	0.5587 (2)	0.0423 (4)
O(4)	0.1216 (2)	0.2685 (1)	0.5049 (2)	0.0425 (4)
O(5)	0.1880 (2)	0.2790 (1)	0.1634 (2)	0.0512 (5)
C(1)	0.2163 (4)	−0.1638 (3)	0.1322 (5)	0.0575 (8)
C(2)	0.3156 (3)	−0.0556 (2)	0.2081 (3)	0.0372 (5)
C(3)	0.4877 (3)	−0.0749 (2)	0.2012 (3)	0.0418 (6)
C(4)	0.5907 (3)	0.0203 (2)	0.2754 (3)	0.0354 (5)
C(5)	0.7800 (3)	−0.0125 (3)	0.2768 (4)	0.0482 (7)
C(6)	0.4617 (5)	0.5592 (3)	0.7725 (5)	0.0587 (9)
C(7)	0.3527 (3)	0.4552 (2)	0.6755 (3)	0.0382 (5)
C(8)	0.1972 (3)	0.4653 (2)	0.7143 (3)	0.0432 (6)
C(9)	0.0934 (3)	0.3703 (2)	0.6354 (3)	0.0363 (5)
C(10)	−0.0568 (3)	0.3817 (2)	0.7075 (4)	0.0491 (7)

Table 2. *Selected geometric parameters* (Å, °)

V(1)—O(1)	1.967 (1)	C(1)—C(2)	1.495 (3)
V(1)—O(2)	1.969 (1)	C(2)—C(3)	1.385 (3)
V(1)—O(3)	1.968 (1)	C(3)—C(4)	1.393 (3)

V(1)—O(4)	1.970 (1)	C(4)—C(5)	1.486 (3)
V(1)—O(5)	1.584 (2)	C(6)—C(7)	1.497 (3)
O(1)—C(2)	1.280 (2)	C(7)—C(8)	1.386 (3)
O(2)—C(4)	1.279 (2)	C(8)—C(9)	1.392 (3)
O(3)—C(7)	1.285 (2)	C(9)—C(10)	1.492 (3)
O(4)—C(9)	1.280 (2)		
O(1)—V(1)—O(2)	87.59 (5)	O(1)—C(2)—C(1)	114.9 (2)
O(1)—V(1)—O(3)	150.13 (6)	O(1)—C(2)—C(3)	124.2 (2)
O(1)—V(1)—O(4)	83.80 (6)	C(1)—C(2)—C(3)	120.9 (2)
O(1)—V(1)—O(5)	104.87 (7)	C(2)—C(3)—C(4)	124.0 (2)
O(2)—V(1)—O(3)	83.84 (6)	O(2)—C(4)—C(3)	123.8 (2)
O(2)—V(1)—O(4)	145.63 (6)	O(2)—C(4)—C(5)	116.2 (2)
O(2)—V(1)—O(5)	107.15 (7)	C(3)—C(4)—C(5)	119.9 (2)
O(3)—V(1)—O(4)	87.29 (6)	O(3)—C(7)—C(6)	115.1 (2)
O(3)—V(1)—O(5)	105.00 (7)	O(3)—C(7)—C(8)	123.9 (2)
O(4)—V(1)—O(5)	107.22 (7)	C(6)—C(7)—C(8)	121.0 (2)
V(1)—O(1)—C(2)	129.0 (1)	C(7)—C(8)—C(9)	124.0 (2)
V(1)—O(2)—C(4)	129.3 (1)	O(4)—C(9)—C(8)	123.8 (2)
V(1)—O(3)—C(7)	128.0 (1)	O(4)—C(9)—C(10)	116.0 (2)
V(1)—O(4)—C(9)	128.8 (1)	C(8)—C(9)—C(10)	120.1 (2)

The unit-cell can be transformed to that used by Dodge, Templeton & Zalkin (1961) by using the matrix: (0 0 1, −1 0 0, 0 −1 0). The scan width was $(1.21 + 0.35\tan\theta)^\circ$ with a θ scan rate of 32° min^{-1} (up to nine scans). Stationary background counts were made at each end of the scan; scan/background time ratio 2:1. All H atoms were visible in a difference map and refined isotropically; the C—H distances are in the range 0.77 (4)–1.01 (4) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: FG1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Tetranuclear Butterfly Cluster of Molybdenum, $[PPh_4]_2[Mo_4I_{11}]$

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Abstract

Bis(tetraphenylphosphonium) undecaiododetramolybdate, $2[PPh_4]^+[Mo_4I_{11}]^{2-}$, was obtained by treating $[Mo_2(MeCN)_8]^{4+}$ with PPN^+I^- in dichloromethane. The four Mo atoms of the anion adopt a 'butterfly' arrangement which can be viewed as a portion of an octahedron with two missing mutually *cis* vertices. Ten of the eleven I atoms are located at the vertices of a cube in which the ideal octahedron would be inscribed; two of them cap the two triangular faces of the Mo_4 buttefly, four bridge the edges and four are terminally coordinated to the metal atoms. The eleventh I atom bridges the two 'wing-tip' metal atoms. The metal–metal distances for four edges of the butterfly wings are in the range 2.533 (3)–2.547 (3) Å, whereas the 'hinge' edge is slightly longer [2.688 (3) Å] and the separation between the two wing tips is 3.051 (3) Å.

Comment

Octahalodimolybdate tetraanions, $[Mo_2X_8]^{4-}$, are known for $X = Cl$ (Brencic & Cotton, 1969) and Br (Brencic, Dobcnik & Segedin, 1974) but have never been reported for $X = I$. The above complexes were prepared by interaction of the acetate complex $Mo_2(OOCCH_3)_4$ or the sulfate complex $(NH_4)_4Mo_2(SO_4)_4.2H_2O$ with aqueous HX solutions. On the other hand, the analogous interaction between $Mo_2(OOCCH_3)_4$ and HI affords, after treatment with $[^nBu_4N]I$, the salt $[^nBu_4N]_2[Mo_4I_{11}]$ (Glicksman & Walton, 1978). There are, however, numerous dimeric complexes of the $Mo_2X_4L_4$ type where $X = I$ (Cotton & Walton, 1982) and the hexaiodo complexes $[Cat]_2[Mo_2I_6(H_2O)_2]$ (Cat = pyH^+, $picH^+$) are also known (Brencic & Segedin, 1978; Brencic & Golic, 1977). We attempted the synthesis of the octaiododimolybdate tetraanion by a new route, *i.e.* the interaction of the trifluoromethylsulfonate (triflate) salt of the acetonitrile complex $[Mo_2(MeCN)_8]$ (Mayer & Abbott, 1983) with tetraphenylphosphonium iodide. The product of the reaction was not a salt of the $[Mo_2I_8]^{4-}$ anion as expected, but a new salt of the previously reported $[Mo_4I_{11}]^{2-}$ anion. It seems therefore that the hypothetical $[Mo_2I_8]^{4-}$ ion might be unstable since all the reactions that are expected to produce it {thermal

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