

The Crystal Structures of α - and β -Tris(2,4-pentanedionato)vanadium(III)*

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Tris(2,4-pentanedionato)vanadium(III), $V(CH_3COCHCOCH_3)_3$, crystallizes in two forms, α in space group $Pcab$ with eight discrete molecules in a cell of dimensions $a_0=15.43$, $b_0=16.60$ and $c_0=13.53$ Å and β in space group $P2_1/n$ with four discrete molecules in a cell of dimensions $a_0=16.34$, $b_0=13.06$, $c_0=8.108$ Å and $\beta=90.00^\circ$. The structures were refined by the full-matrix least-squares method by use of three-dimensional Mo $K\alpha$ data to $R=0.066$ and 0.102 for the α and β forms, respectively. The mean values of chemically equivalent interatomic separations in the two forms are 1.981 Å for V–O, 1.259 Å for O–C, 1.386 Å for ring C···C and 1.518 Å for C–C(methyl). The slight trigonal distortion of the octahedron formed by the oxygen atoms about the vanadium atom is due to the mean O–V–O intraring angle of 87.7° .

Introduction

The crystal structures for the trivalent metal 2,4-pentanedione compounds appear to be grouped into several isomorphous series (Astbury, 1926). The structural parameter responsible for these different packing arrangements probably is the metal–oxygen separation and can best be reflected in the molar volume; hence, for example, the complexes of Al, Mn, Co, Cr, and one allotrope of Ga with molar volumes <430 Å³ belong to a monoclinic, $P2_1/c$, isomorphous set while those of Fe, In, Sc and another allotrope of Ga with molar volumes >430 Å³ were reported to belong to two different orthorhombic space groups. One form of tris(2,4-pentanedionato)vanadium(III), hereafter α -V(Acac)₃, with a molar volume of 433 Å³ has been found to be isomorphous with the iron complex; for the other form, β -V(Acac)₃, no complete structure study has yet been reported. In both of these polymorphic forms the metal–oxygen bond is shorter and presumably more covalent than that found in the iron complex (Iball & Morgan, 1967).

Experimental

Two methods were used to synthesize the compound. The first involved the electrolytic reduction of $VOSO_4$ to $V_2(SO_4)_3$ and subsequent reaction with 2,4-pentanedione (HAcac) in the presence of mild alkali (sodium carbonate). The crude precipitate was recrystallized from benzene, methanol or 2,4-pentanedione. Chlorinated solvents ($CHCl_3$, CH_2Cl_2) were found to

encourage oxidation to $VO(Acac)_2$. No special precautions were taken to exclude air, and there was no appreciable oxidation in the solvents first named. A second method was essentially that of Grdenic & Korper-Colig (1964), except that the zinc derivative was separated from the vanadium one by extraction with petroleum spirit (Phillips 60–90° cut) in a Soxhlet apparatus. The melting point was 186–189° (reported 185–189, Morgan & Moss, 1913). However, it is obvious that some oxidation takes place during the melting process. Analysis for vanadium was determined by weighing V_2O_5 after the compound was heated with HNO_3 ; for $V(C_5H_7O_2)_3$ calculated V content is 14.63%, found 14.56%. The density, determined by the flotation technique using CCl_4 and alcohol was found to be 1.33 g.cm⁻³; with $z=8$ and $Vol=3467$ Å³, the calculated value for the α form is 1.334 g.cm⁻³.

The symmetry of the lattice was verified by Weissenberg and precession photographs taken with Cu $K\alpha$ and Mo $K\alpha$ radiation. On several batches of crystals (designated the α form), systematic absences of $0kl$ for l odd, of $h0l$ for h odd and of $hk0$ for k odd unequivocally established the space group as $Pcab$, cell edges selected to conform to Donnay's (1943) rules. A comparison of intensities quickly showed that this compound is probably isostructural with the Fe^{III} analogue. Other batches of crystals were first thought to be of orthorhombic symmetry (belonging to space group $Pnm2$) and to be isostructural with Ga, In and Sc compounds reported by Astbury (1926). However, a few discrepancies were noted between hkl and $hk\bar{l}$ intensities. More careful observations on several crystal specimens suggested the symmetry to be monoclinic. The variation from crystal to crystal of the intensity ratio for certain pairs of hkl and $hk\bar{l}$ reflections (those which had large intensity differences) suggested that

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intimate twinning with rather small domain size occurs in this form. With systematic absences of $h0l$ for $h+l$ odd and $0k0$ for k odd, the space group is established to be $P2_1/n$. The following lattice constants were obtained by least-squares fit of the diffractometer settings using Mo $K\alpha$ radiation (λ for $K\alpha_1 = 0.70926 \text{ \AA}$):

α -V(Acac) ₃	β -V(Acac) ₃
$a_0 = 15.43 (2)$	$16.34 (1)$
$b_0 = 16.60 (2)$	$13.06 (1)$
$c_0 = 13.53 (1)$	$8.108 (5)$
	$\beta = 90.00 (3)^\circ$

Three-dimensional Mo $K\alpha$ intensity data were measured by use of the θ - 2θ scan technique on a Picker diffractometer equipped with an E & A full-circle Eulerian orienter. A Datex automatic control module was used for setting the angles of the 3061 possible intensity data (up to $60^\circ 2\theta$) investigated for the α form. Only 1361 of these measured intensity data were considered observed; the remaining 1700 were measured to be less than 3σ ($\sigma = \sqrt{N_{sc} + K(N_{b1} + N_{b2})}$, where N_{sc} , N_b and K are the total scan count, background counts and scan time divided by total background time, respectively) and, hence, assigned a value equal to 3σ , and considered as unobserved in subsequent calculations. For the β form, 3043 intensity data were meas-

ured of which 1703 and 1340 were considered observed and unobserved, respectively. The crystal specimen used for data collection was selected from the many photographed on the basis of showing the largest intensity differences between hkl and $h\bar{k}l$. Absorption corrections were considered unnecessary for either crystal; for the α form, the crystal was of dimensions $0.27 \times 0.20 \times 0.55 \text{ mm}$ ($\mu = 8.8 \text{ cm}^{-1}$ for Mo $K\alpha$) while that for the β form was $0.18 \times 0.18 \times 0.35 \text{ mm}$; both were mounted on the long direction.

Lorentz and polarization factors were applied and structure factors calculated by use of neutral scattering factors from Table 3.3.1A (p.202) of *International Tables for X-ray Crystallography* (1962). The dispersion correction for vanadium was not included. The function, $\sum w(F_o - F_c)^2$, was minimized for our least-squares refinements. Weights were assigned from counting statistics with no additional error included for instrument instability; unobserved reflections were assigned zero weight if $|F_o| > |F_c|$.

Structure determinations

For the α form a three-dimensional Patterson function was consistent with vanadium atoms at 0.140, 0.245, 0.270; the subsequent Fourier synthesis yielded atomic positions very similar to those for the iron complex.

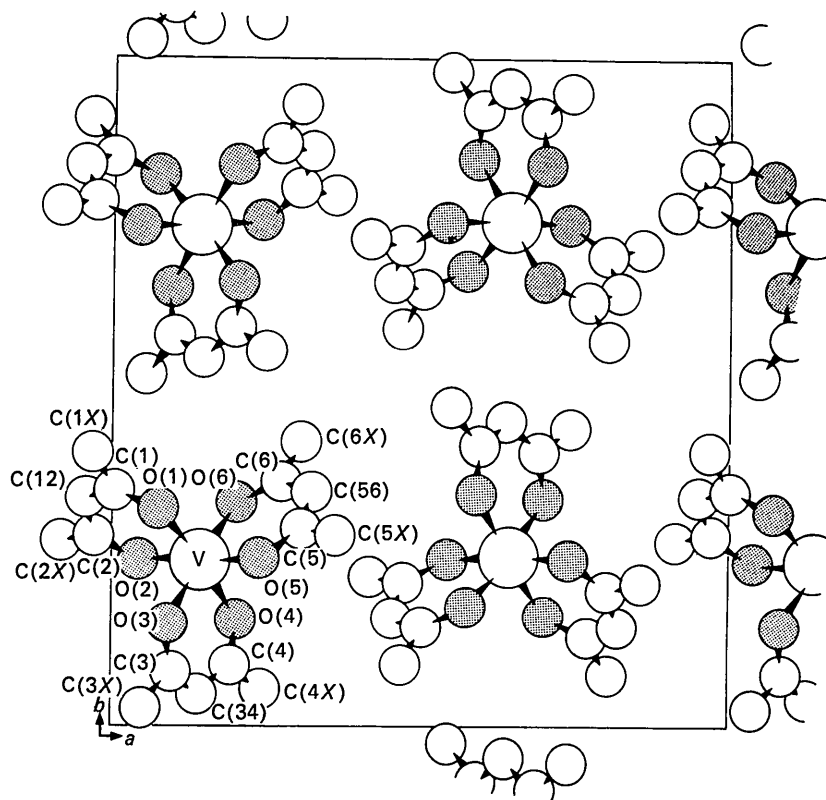


Fig.1. The labeling scheme and partial molecular arrangement for α -tris(2,4-pentanedionato)vanadium(III). The projection viewed along the c axis only includes atoms of molecules centered near z equal to $\frac{1}{4}$.

Four cycles of least-squares refinement with isotropic thermal parameters resulted in an R value, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, of 0.114; subsequent refinement with anisotropic thermal parameters reduced R to 0.081. A three-dimensional difference synthesis yielded the locations of all the hydrogen atoms (Table 1). Six further cycles of least-squares refinement resulted in $R = 0.066$; the ratios of average shifts to estimated errors and of maximum shift to estimated error were 0.01 and 0.07, respectively. Final coordinates are given in Table 2. Observed and calculated structure factors may be obtained from the authors. The labeling scheme and molecular arrangement are shown in Fig. 1.

Table 1. *Hydrogen coordinates* ($B = 4.0 \text{ \AA}^2$)

	x	y	z
H (12)	-0.093	0.380	0.270
H (34)	0.130	-0.010	0.240
H (56)	0.380	0.390	0.300
H (X11)	-0.070	0.450	0.390
H (X12)	0.020	0.460	0.420
H (X13)	-0.010	0.370	0.480
H (X21)	-0.070	0.310	0.030
H (X22)	-0.070	0.210	0.060
H (X23)	-0.150	0.290	0.100
H (X31)	0.010	0.000	0.330
H (X32)	0.070	-0.010	0.400
H (X33)	0.000	0.060	0.405
H (X41)	0.210	0.030	0.045
H (X42)	0.290	0.090	0.080
H (X43)	0.290	0.020	0.105
H (X51)	0.370	0.300	0.425
H (X52)	0.365	0.235	0.480
H (X53)	0.390	0.330	0.480
H (X61)	0.370	0.410	0.120
H (X62)	0.250	0.470	0.120
H (X63)	0.335	0.450	0.160

For the β form a three-dimensional Patterson function indicated vanadium atoms to be situated at 0.25,

0.01, 0.04; the subsequent Fourier synthesis yielded light atom positions which could be assigned to two different molecular packings. Subsequent difference syntheses and least-squares refinement of partial sets of atoms for both models quickly eliminated one choice; the remaining model was refined by use of anisotropic thermal parameters to an R value of 0.124. At this point it was noted that for pairs of hkl and $hk\bar{l}$ which involved very strong and weak observed values, the weak reflection always was assigned an observed value larger than the calculated value. There were 193 such pairs in which $I_{\text{strong}} > 3I_{\text{weak}}$; these pairs were used to obtain the amount of satellite twin possibly present in the crystal specimen used for data collection. The average volume of the suggested twin is near 10% (21 pairs indicated no twin present; of these 4 were discarded from the averaging procedure). The total set of intensity data was corrected assuming such a satellite and subjected to two final cycles of least-squares refinement (weights were not altered from those previously assigned). The resulting R is 0.102. A three-dimensional difference synthesis did not show any anomalous peaks; the small peaks present did not always yield consistent hydrogen positions and, hence, none were included in our structure determination. Final coordinates are given in Table 3 and the labeling scheme and molecular arrangement are shown in Fig. 2.

Discussion

The molecular packings of $\text{Fe}(\text{Acac})_3$ and $\alpha\text{-V}(\text{Acac})_3$ are very similar as had been indicated by comparison of the corresponding intensity data. The mean values of chemically equivalent interatomic separations in the α form (Table 4) are 1.979 \AA for V-O, 1.256 \AA for O-C, 1.383 \AA for ring C...C and 1.518 \AA for C-C

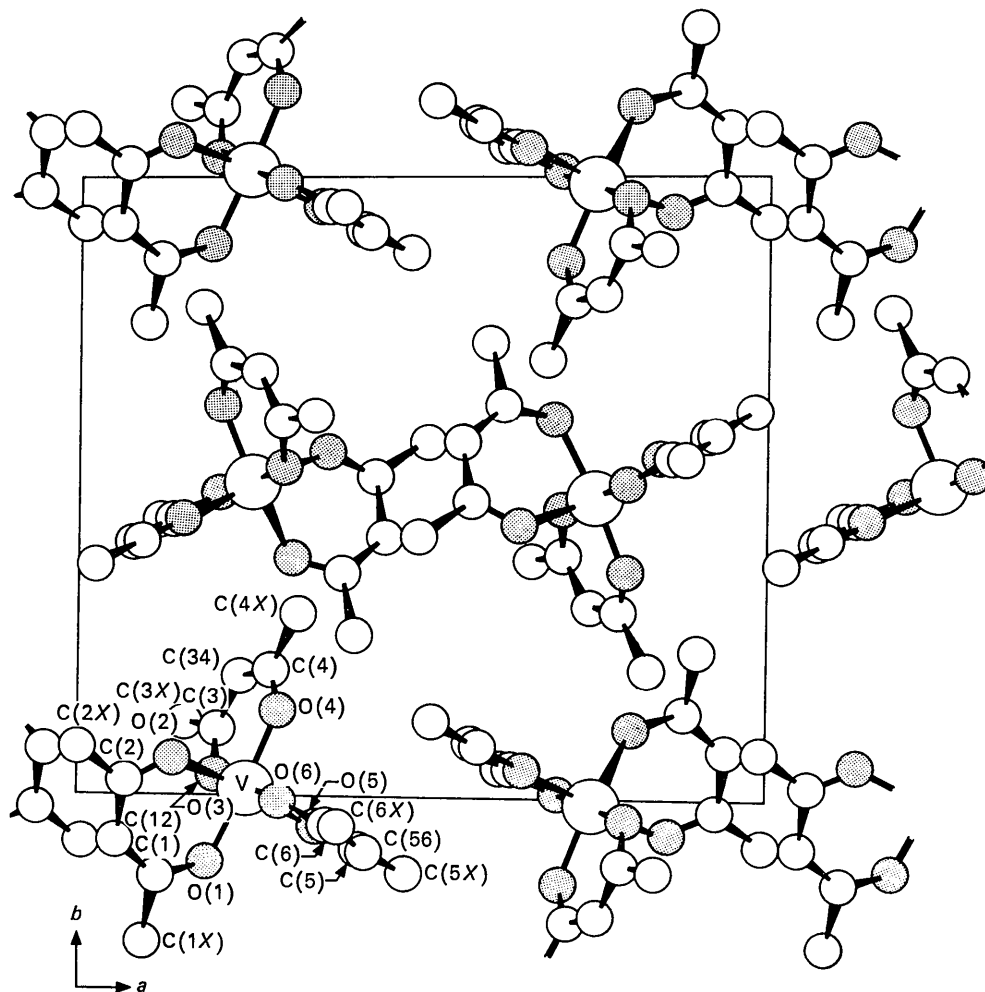
Table 2. *Final atomic coordinates and anisotropic temperature factors for $\alpha\text{-V}(\text{Acac})_3$*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V	0.14173 (6)	0.24556 (6)	0.26692 (6)	3.46 (3)	3.27 (3)	2.66 (3)	-0.37 (5)	0.43 (3)	-0.31 (4)
O(1)	0.0764 (3)	0.3214 (3)	0.3514 (3)	4.7 (2)	5.4 (2)	3.5 (2)	1.2 (3)	0.5 (2)	-1.1 (2)
O(2)	0.0447 (2)	0.2491 (4)	0.1716 (3)	3.1 (2)	6.2 (2)	4.0 (2)	-0.3 (2)	0.3 (1)	-0.2 (2)
O(3)	0.0913 (3)	0.1527 (3)	0.3364 (3)	5.6 (2)	4.7 (2)	4.0 (2)	-1.4 (2)	1.4 (2)	-0.0 (2)
O(4)	0.2017 (3)	0.1673 (3)	0.1797 (3)	4.4 (2)	4.8 (2)	3.9 (2)	0.5 (2)	1.4 (2)	-0.4 (2)
O(5)	0.2385 (3)	0.2494 (4)	0.3646 (3)	5.3 (2)	5.7 (2)	2.8 (2)	-0.0 (3)	-0.1 (1)	0.9 (2)
O(6)	0.2006 (3)	0.3324 (3)	0.1933 (3)	5.9 (3)	4.4 (2)	3.4 (2)	-1.4 (2)	-0.4 (2)	1.3 (2)
C(1)	0.0031 (5)	0.3517 (4)	0.3376 (5)	6.0 (4)	3.2 (5)	4.3 (3)	0.8 (3)	1.0 (3)	0.0 (2)
C(2)	-0.0246 (5)	0.2858 (5)	0.1777 (5)	4.9 (3)	6.5 (4)	3.2 (3)	-1.0 (3)	0.5 (2)	0.6 (2)
C(12)	-0.0484 (5)	0.3392 (5)	0.2539 (6)	5.9 (4)	6.1 (4)	4.0 (3)	1.9 (3)	0.5 (3)	0.0 (3)
C(1X)	-0.0274 (8)	0.4083 (6)	0.4195 (7)	12.1 (8)	7.0 (5)	6.2 (5)	4.1 (5)	1.4 (5)	-1.4 (4)
C(2X)	-0.0860 (5)	0.2770 (6)	0.0904 (6)	3.6 (3)	12.0 (8)	3.7 (3)	0.9 (4)	-0.2 (2)	0.7 (4)
C(3)	0.0956 (6)	0.0791 (5)	0.3134 (6)	7.7 (5)	3.9 (3)	5.6 (4)	-1.3 (3)	0.4 (4)	1.4 (3)
C(4)	0.1900 (5)	0.0921 (4)	0.1707 (5)	4.2 (3)	4.9 (3)	5.3 (4)	1.4 (3)	-0.4 (3)	-1.2 (3)
C(34)	0.1370 (7)	0.0477 (4)	0.2316 (7)	8.8 (5)	3.2 (3)	7.2 (5)	-1.6 (3)	1.5 (5)	-1.2 (3)
C(3X)	0.0459 (7)	0.0240 (5)	0.3830 (7)	10.5 (7)	4.9 (4)	8.3 (6)	-1.3 (4)	1.8 (5)	1.9 (4)
C(4X)	0.2392 (7)	0.0525 (6)	0.0887 (7)	8.5 (6)	7.8 (5)	6.6 (5)	2.9 (4)	0.3 (4)	-3.7 (4)
C(5)	0.3035 (5)	0.2953 (5)	0.3669 (5)	4.4 (3)	5.6 (4)	3.5 (3)	-0.3 (3)	-0.2 (3)	-1.6 (3)
C(6)	0.2726 (5)	0.3643 (4)	0.2120 (5)	5.5 (4)	5.7 (3)	4.5 (3)	-1.6 (3)	0.7 (3)	0.7 (3)
C(56)	0.3220 (6)	0.3497 (6)	0.2958 (6)	5.5 (4)	6.7 (4)	6.0 (4)	-2.0 (4)	-0.7 (3)	0.7 (4)
C(5X)	0.3607 (7)	0.2859 (6)	0.4580 (6)	7.3 (5)	11.5 (7)	5.0 (4)	0.1 (5)	-3.4 (4)	-0.0 (4)
C(6X)	0.3021 (7)	0.4233 (6)	0.1330 (8)	7.8 (6)	8.1 (6)	9.2 (6)	-3.3 (5)	-0.1 (5)	4.2 (5)

Anisotropic thermal parameters are of the form $\exp(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^*)$.

Table 3. Final atomic coordinates and anisotropic temperature factors for β -V(Acac)₃

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
V	0.2490 (1)	0.0096 (1)	0.0432 (2)	3.25 (5)	2.64 (5)	2.46 (4)	0.08 (5)	0.02 (9)	0.12 (6)
O(1)	0.1959 (4)	-0.1279 (5)	0.0447 (8)	4.4 (3)	3.6 (1)	4.0 (3)	-0.0 (3)	0.7 (3)	0.2 (2)
O(2)	0.1477 (5)	0.0636 (5)	0.1479 (9)	5.2 (4)	4.2 (1)	5.1 (3)	0.6 (3)	-0.3 (3)	-0.6 (2)
O(3)	0.2087 (4)	0.0355 (5)	-0.1830 (7)	5.8 (3)	4.4 (2)	3.1 (2)	-0.4 (3)	-1.3 (4)	-0.1 (2)
O(4)	0.2975 (4)	0.1475 (5)	0.0390 (7)	5.4 (3)	3.8 (1)	3.2 (2)	-1.3 (3)	-0.7 (3)	0.3 (2)
O(5)	0.3485 (4)	-0.0571 (5)	-0.0488 (8)	3.9 (3)	5.3 (2)	3.8 (3)	0.8 (3)	0.5 (3)	-0.6 (2)
O(6)	0.2978 (4)	-0.0139 (5)	0.2667 (7)	4.1 (3)	5.3 (2)	3.4 (2)	0.7 (3)	-0.0 (3)	0.7 (2)
C(1)	0.1249 (6)	-0.1532 (7)	0.0883 (10)	3.7 (4)	3.5 (3)	3.2 (3)	-0.2 (3)	0.8 (3)	0.6 (3)
C(2)	0.0807 (6)	0.0204 (8)	0.1774 (11)	4.1 (4)	5.5 (4)	3.1 (3)	0.1 (4)	-1.0 (3)	0.2 (3)
C(3)	0.2099 (5)	0.1186 (7)	-0.2667 (10)	3.5 (3)	3.8 (3)	2.9 (3)	0.1 (3)	0.2 (3)	-0.2 (3)
C(4)	0.2871 (6)	0.2197 (7)	-0.0709 (11)	3.5 (4)	3.9 (4)	4.2 (4)	0.3 (3)	1.1 (3)	0.0 (2)
C(5)	0.4080 (6)	-0.0973 (8)	0.0208 (13)	3.6 (4)	4.7 (5)	5.7 (4)	0.4 (4)	1.6 (3)	1.1 (4)
C(6)	0.3614 (6)	-0.0586 (8)	0.3056 (12)	5.3 (5)	5.0 (5)	3.5 (3)	0.2 (4)	-1.0 (3)	0.9 (4)
C(12)	0.0670 (7)	-0.0858 (10)	0.1539 (12)	4.9 (5)	7.7 (6)	3.4 (3)	-1.0 (5)	0.1 (3)	-0.4 (4)
C(34)	0.2468 (6)	0.2088 (8)	-0.2163 (9)	5.4 (5)	4.9 (5)	2.3 (3)	1.3 (4)	-0.8 (3)	0.0 (3)
C(56)	0.4168 (8)	-0.1020 (10)	0.1912 (17)	5.2 (5)	6.8 (6)	7.0 (5)	1.0 (5)	-0.7 (4)	0.8 (6)
C(1X)	0.1040 (9)	-0.2636 (9)	0.0713 (17)	7.9 (8)	5.3 (6)	7.3 (6)	-2.3 (6)	1.1 (5)	-0.7 (5)
C(2X)	0.0099 (7)	0.0872 (11)	0.2530 (13)	5.4 (5)	8.9 (7)	3.7 (4)	2.5 (6)	-0.8 (4)	-0.7 (5)
C(3X)	0.1690 (8)	0.1154 (9)	-0.4376 (12)	6.2 (6)	6.3 (7)	3.8 (4)	1.1 (5)	-0.7 (4)	0.8 (5)
C(4X)	0.3279 (7)	0.3194 (8)	-0.0273 (13)	6.2 (6)	3.6 (6)	5.2 (4)	-1.0 (5)	-0.5 (4)	0.8 (4)
C(5X)	0.4725 (8)	-0.1427 (11)	-0.0896 (18)	5.4 (7)	8.3 (8)	8.1 (7)	2.2 (6)	3.3 (5)	0.7 (6)
C(6X)	0.3789 (9)	-0.0616 (11)	0.4905 (14)	8.1 (8)	7.9 (8)	3.8 (4)	-0.6 (6)	-1.3 (4)	2.5 (5)

Fig. 2. The labeling scheme and molecular arrangement for β -tris(2,4-pentanedionato)vanadium(III). The projection is viewed along the *c* axis.

(methyl). These nonmetal values (as well as those found in the β form) compare favorably with the corresponding values determined for the iron complex (1.258, 1.377 and 1.530 Å; Iball & Morgan, 1967) or for other metal acetylacetonates (Lingafelter & Braun, 1967). The octahedron formed by oxygen atoms about the vanadium atom is trigonally distorted in both forms owing to the mean O–V–O intraring angle of 87.7°.

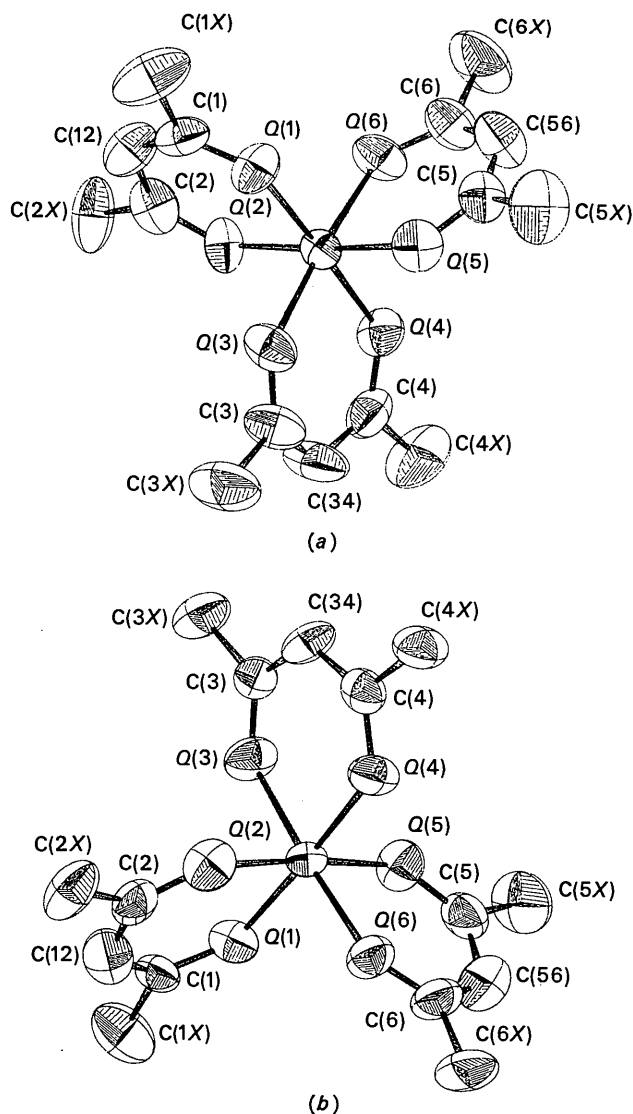
Table 4. *Intramolecular bond lengths and angles*

	α form	β form
V–O(1)	1.977 (8) Å	1.983 (8) Å
V–O(2)	1.977	1.997
V–O(3)	1.967	1.980
V–O(4)	1.984	1.966
V–O(5)	1.995	1.976
V–O(6)	1.974	1.992
Average	1.979	1.982
O(1)–C(1)	1.253 (14)	1.261 (16)
O(2)–C(2)	1.235	1.254
O(3)–C(3)	1.263	1.276
O(4)–C(4)	1.268	1.301
O(5)–C(5)	1.261	1.240
O(6)–C(6)	1.258	1.241
Average	1.256	1.262
C(1)–C(12)	1.399 (19)	1.391 (21)
C(2)–C(12)	1.408	1.401
C(3)–C(34)	1.379	1.383
C(4)–C(34)	1.376	1.368
C(5)–C(56)	1.350	1.394
C(6)–C(56)	1.387	1.412
Average	1.383	1.391
C(1)–C(1X)	1.528 (21)	1.480 (23)
C(2)–C(2X)	1.520	1.579
C(3)–C(3X)	1.520	1.533
C(4)–C(4X)	1.497	1.502
C(5)–C(5X)	1.525	1.490
C(6)–C(6X)	1.520	1.526
Average	1.518	1.518
O(1)–V–O(2)	88.4 (6)°	86.7 (6)°
O(3)–V–O(4)	87.5	87.9
O(5)–V–O(6)	88.1	87.3
V–O(1)–C(1)	129.0 (8)	130.7 (8)
V–O(2)–C(2)	128.9	130.7
V–O(3)–C(3)	128.3	129.0
V–O(4)–C(4)	129.5	138.6
V–O(5)–C(5)	129.1	131.7
V–O(6)–C(6)	127.8	129.2
O(1)–C(1)–C(1X)	114.6 (9)	116.0 (9)
O(2)–C(2)–C(2X)	114.1	118.0
O(3)–C(3)–C(3X)	113.7	116.7
O(4)–C(4)–C(4X)	115.6	114.6
O(5)–C(5)–C(5X)	114.8	117.2
O(6)–C(6)–C(6X)	113.2	114.6
C(1)–C(12)–C(2)	122.6 (9)	125.2 (9)
C(3)–C(34)–C(4)	123.6	123.9
C(5)–C(56)–C(6)	125.7	124.9
O(1)–C(1)–C(12)	125.1 (9)	123.5 (9)
O(2)–C(2)–C(12)	125.8	122.9
O(3)–C(3)–C(34)	126.0	125.0
O(4)–C(4)–C(34)	123.7	125.0
O(5)–C(5)–C(56)	123.7	122.4
O(6)–C(6)–C(56)	125.2	124.3

Table 4 (cont.)

	α form	β form
C(12)–C(1)–C(1X)	120.2 (9)	120.5 (9)
C(12)–C(2)–C(2X)	120.3	119.0
C(34)–C(3)–C(3X)	120.2	118.3
C(34)–C(4)–C(4X)	120.7	120.4
C(56)–C(5)–C(5X)	121.5	120.4
C(56)–C(6)–C(6X)	121.5	121.2

Iball & Morgan concluded that the mean value of the iron–oxygen distance in $\text{Fe}(\text{Acac})_3$ was more compatible with an ionic than a covalent bond. For example, the sum of Pauling's (1960) values for trivalent octahedral ionic radii (p. 518; iron, 0.64; oxygen, 1.35 Å) is in good agreement with the mean observed value of 1.992 Å. For $\text{V}(\text{Acac})_3$, the corresponding

Fig. 3. ORTEP views of the molecules nearly along the three-fold axes. (a) α form, (b) β form.

radii (vanadium, 0.74 Å) total about 0.10 Å more than those for the Fe–O separation yet the observed mean value for the V–O separation is 1.981 Å. This value suggests that the V–O bond is more covalent than the corresponding Fe–O bond. (Values for V–O separation in vanadyl(IV) bisacetylacetonate and bisbenzoylacetone have been determined to be near 1.97 Å by Pfluger (1968); no other trivalent V–O separations are known to the authors.)

For two of the three chelate rings, the vanadium ion in the α form lies in the least-squares plane formed by the five atoms of the 2,4-pentanedione ring. Only the ring atoms are included in calculation of the least-squares plane because steric effects from crystal packing appear systematically to affect methyl groups in isomorphous sets of 2,4-pentanedione compounds (Morosin, 1967). A comparison of the corresponding values found in $\text{Fe}(\text{Acac})_3$ and $\alpha\text{-V}(\text{Acac})_3$ is given in Table 5. In both of these, it is clear that the metal ion lies off the least-squares plane in only one of the rings. For $\beta\text{-V}(\text{Acac})_3$ the metal ion lies off the plane for all three chelate rings. Since the structures of the Ga, In or Sc analogs have not been reported, one is not able to invoke packing effects for the β form.

Fig. 3 illustrates the anisotropic thermal parameters for the two forms of $\text{V}(\text{Acac})_3$. In general the root mean square amplitudes are greater along directions perpendicular to the planes formed by the chelate rings than along chemical bonds. However, short contact separations between C(3x) and C(3x) on different molecules in $\alpha\text{-V}(\text{Acac})_3$ and between C(2x) and C(12) as well as between C(2x) and C(3x) on different molecules

in $\beta\text{-V}(\text{Acac})_3$ account for part of the departures from the expected directions of the thermal ellipsoids.

Table 5. *Distance of metal from ideal ligand plane*

	Metal	A*	B*	σ^*
$\alpha\text{-V}(\text{Acac})_3^*$	0.003	0.010	0.015	0.016
	0.227	0.045	0.151	0.029
	0.004	0.111	0.134	0.026
$\text{Fe}(\text{Acac})_3$	0.001	0.027	0.052	0.006
	0.266	0.088	0.208	0.016
	0.081	0.070	0.139	0.025
$\beta\text{-V}(\text{Acac})_3$	0.089	0.001	0.049	0.012
	0.173	0.032	0.072	0.006
	0.075	0.038	0.063	0.004

* $\text{Acac} = \text{C}_5\text{H}_7\text{O}_2$; A is the methyl carbon closer to least-squares plane; B other methyl-carbon; and σ is the standard deviation of the atoms (those defining the plane) from the least-squares plane.

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The Crystal Structure of Thiamine Pyrophosphate

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An X-ray crystal structure analysis of triclinic thiamine pyrophosphate is reported. The space group is $P\bar{1}$ with $a = 13.42$, $b = 12.24$, $c = 15.57$ Å, $\alpha = 56^\circ 20'$, $\beta = 95^\circ 46'$, $\gamma = 90^\circ 25'$ and with two molecules in the asymmetric unit. The structure and molecular conformation differ from those of monoclinic thiamine pyrophosphate hydrochloride. The parameters of both the thiamine and pyrophosphate portions of the molecule are in general agreement with parameters of related crystal structures. The structure possesses layer-type characteristics and there is some evidence for end-to-end hydrogen bonding of the pyrophosphate groups, the oxygen atoms of which are in the staggered conformation.

The structure was solved by use of the three-dimensional Patterson function and successive partial Fourier syntheses of electron density, and refined to an R value of 27.9% on 4920 non-zero observed reflexions.

Introduction

Thiamine, or vitamin B_1 , is an essential dietary factor for all animals. In man its deficiency is the cause of

the disease beriberi. Thiamine, however, functions in its coenzyme form, cocarboxylase or thiamine pyrophosphate, (TPP). The structural formula and conventional thiamine ring numbering is shown below.