metal-organic compounds

Redetermination of bis(acetylacetonato)-oxidopyridinevanadium(IV)

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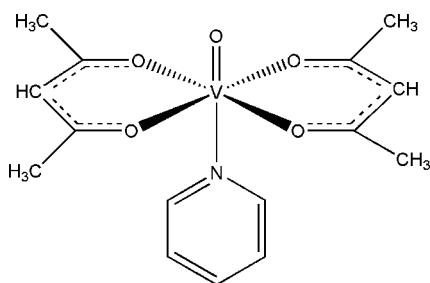Correspondence e-mail: rburow@ewald.base.ufsm.br

The crystal structure of the title compound, $[VO(C_5H_7O_2)_2(C_5H_5N)]$, has been reported previously [Meicheng, Lifeng & Youqi (1984). *Kexue Tongbao*, **29**, 759–764], with an R value of 0.13. The current redetermination shows a significant improvement in the precision of the geometric parameters. The V atom binds five O atoms and one N atom from the pyridine ligand in a distorted octahedral configuration; the acetylacetonate anions act as bidentate ligands. A crystallographic twofold axis passes through the V, vanadyl O, and pyridine N and *para*-C atoms.

Related literature

For a related structure, see: Meicheng *et al.* (1984). For related literature, see: Allen (2002).

Experimental

Crystal data

$[V(C_5H_7O_2)_2O(C_5H_5N)]$	$V = 1701.54$ (12) Å^3
$M_r = 344.25$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 7.9121$ (3) Å	$\mu = 0.60$ mm^{-1}
$b = 15.5258$ (7) Å	$T = 296$ (2) K
$c = 14.2523$ (6) Å	$0.35 \times 0.35 \times 0.25$ mm
$\beta = 103.621$ (3)°	

Data collection

Bruker APEX II area-detector diffractometer	11650 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)	2595 independent reflections
	1837 reflections with $I > 2\sigma(I)$
$T_{min} = 0.903$, $T_{max} = 1$	$R_{int} = 0.032$
(expected range = 0.776–0.860)	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	104 parameters
$wR(F^2) = 0.116$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
2595 reflections	$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—V1	2.422 (2)	O2—V1	1.9918 (11)
O1—V1	1.5976 (18)	O3—V1	1.9997 (11)
C3—O2—V1	127.66 (11)	O1—V1—O3	98.30 (4)
C1—O3—V1	127.44 (11)	O2—V1—O3	89.55 (5)
O1—V1—O2	99.92 (4)	O2^i—V1—O3	87.60 (5)
O2—V1—O2^i	160.16 (8)	O1—V1—N1	180

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

Data collection: *APEX2*, *COSMO* and *BIS* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2476).

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supplementary materials

Redetermination of bis(acetylacetonato)oxidopyridinevanadium(IV)

R. M. S. da Silva, C. C. Spiazzi, R. Bortolotto and R. A. Burrow

Comment

The crystal structure of the title compound, $VO(C_5H_7O)_2C_5H_5N$, was determined previously by (Meicheng *et al.*, 1984). The original structure refinement converged with $R1 = 0.13$ [CUCWUS; Cambridge Structural Database (CSD, Version 5.28, update of January 2007; Allen, 2002)]. The current redetermination shows a significant improvement in the precision of the geometric parameters. A low temperature experiment was attempted, but the crystal quickly powders under a cold nitrogen stream. One half-molecule is found in the asymmetric unit; the complete molecule is generated by a crystallographic 2 fold axis which passes through atoms O1, V1, N1 and C8. The geometry of the hexacoordinate V atom can be regarded as distorted octahedral with the two acetylacetonato ligands chelating in the equatorial plane, and the vandyl O and the pyridinal N atoms in axial positions (Fig. 1). The V1 atom is centered 0.3160 (10) Å out of the plane formed by four coordinated oxygen atoms, in the direction of the apical O1 atom. The V=O distance is 1.5976 (18) Å in good agreement with ranges observed for other VO_5N octahedral found in the Cambridge Structural Database (CSD, Version 5.28, update of January 2007; Allen, 2002)] (V=O 1.598 (11) Å for 21 observations), the *cisoid* angles (O–V–O and O–V–N) being 80.08 (4) – 99.92 (4)°, and *transoid* angles (O–V–O and O–V–N) being 160.16 (8) – 180° (Table 1). The molecules packs around a crystallographic twofold screw axis, parallel to the crystallographic *b*-axis (Fig. 2).

The thermal gravimetric analysis (TGA) of **1** shows a loss of one molecule of pyridine (exp. 22.03%, calc. 22.97%) at 334.98 K, followed by the loss of $C_{10}H_{16}O_5$(exp. 64.41%, calc. 62.23%)at 438.45 K. The residual weight for the whole process (exp. 13.56%, calc. 14.80%) is in good agreement assuming V as the final end product.

Experimental

The title compound was synthesized by refluxing VO(acac)2 (1.00 g, 3.68 mmol) dissolved pyridine (15 ml) for 2 h. After cooling to room temperature, 80 ml of diethyl ether was added. Light green single crystals of the compound were obtained by slow evaporation of the solution at room temperature over several days in a dessecator. Yield (crystals): 0.13 g (10.15%).

Refinement

All H atoms on were refined using a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for the methine C atoms and C—H = 0.96 Å and $U_{iso} = 1.5U_{eq}(C)$ for the methyl C atoms.
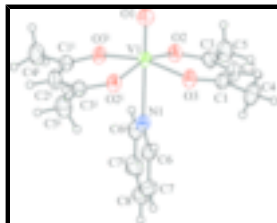
supplementary materials

Figures

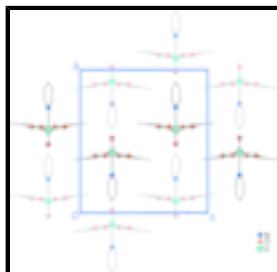Fig. 1. The molecular structure with 30% probability ellipsoids. [Symmetry code: (i) $1 - x$, y, $1.5 - z$.]

Fig. 2. Part of the crytal structure viewed perpendicular to the bc plane. The phenyl groups are represented as solid grey lines. Hydrogen atoms omitted for sake of clarity.

bis(acetylacetonato)oxidopyridinevanadium(IV)

Crystal data

$[V(C_5H_7O_2)_2O(C_5H_5N)]$	$F_{000} = 716$
$M_r = 344.25$	$D_x = 1.344$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 2628 reflections
$a = 7.9121$ (3) Å	$\theta = 2.9–24.1°$
$b = 15.5258$ (7) Å	$\mu = 0.60$ mm^{-1}
$c = 14.2523$ (6) Å	$T = 296$ (2) K
$\beta = 103.621$ (3)°	Trapezoid, blue–green
$V = 1701.54$ (12) Å^3	$0.35 \times 0.35 \times 0.25$ mm
$Z = 4$	

Data collection

Bruker APEX II area-detector diffractometer	1837 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.032$
$T = 296(2)$ K	$\theta_{max} = 30.4°$
ϕ and ω scans	$\theta_{min} = 2.9°$
Absorption correction: multi-scan (SADABS; Bruker, 2006)	$h = -11 \rightarrow 11$
$T_{min} = 0.903$, $T_{max} = 1$	$k = -22 \rightarrow 20$
11650 measured reflections	$l = -20 \rightarrow 20$
2595 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.039$	H-atom parameters constrained
$wR(F^2) = 0.116$	$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 0.0762P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
2595 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
104 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.8337 (2)	0.61290 (12)	0.88998 (13)	0.0543 (4)
C2	0.7518 (2)	0.62217 (15)	0.96641 (14)	0.0663 (5)
H2	0.8226	0.6322	1.0275	0.08*
C3	0.5742 (2)	0.61768 (12)	0.95867 (12)	0.0525 (4)
C4	1.0287 (2)	0.61760 (18)	0.91047 (17)	0.0838 (7)
H4A	1.0753	0.5607	0.9086	0.126*
H4B	1.0731	0.6421	0.9733	0.126*
H4C	1.0623	0.6529	0.8627	0.126*
C5	0.5044 (3)	0.62994 (17)	1.04695 (13)	0.0761 (6)
H5A	0.4164	0.6738	1.0348	0.114*
H5B	0.5972	0.647	1.1001	0.114*
H5C	0.4551	0.5768	1.0624	0.114*
C6	0.6215 (2)	0.78243 (13)	0.71999 (13)	0.0592 (5)
H6	0.707	0.7525	0.6985	0.071*
C7	0.6260 (3)	0.87100 (15)	0.71941 (14)	0.0755 (6)
H7	0.7133	0.9	0.6985	0.091*
C8	0.5	0.91579 (19)	0.75	0.0835 (10)
H8	0.5	0.9757	0.75	0.1*

N1	0.5	0.73721 (13)	0.75	0.0495 (4)
O1	0.5	0.47833 (11)	0.75	0.0607 (4)
O2	0.46038 (14)	0.60333 (8)	0.88081 (8)	0.0530 (3)
O3	0.75487 (14)	0.59983 (9)	0.80249 (9)	0.0544 (3)
V1	0.5	0.58123 (3)	0.75	0.04534 (15)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0421 (8)	0.0563 (10)	0.0592 (11)	0.0013 (7)	0.0014 (7)	−0.0033 (8)
C2	0.0509 (10)	0.0910 (15)	0.0500 (10)	−0.0003 (10)	−0.0018 (8)	−0.0085 (10)
C3	0.0576 (9)	0.0538 (10)	0.0444 (9)	0.0013 (8)	0.0087 (7)	0.0035 (7)
C4	0.0411 (9)	0.115 (2)	0.0879 (16)	0.0009 (11)	0.0001 (9)	−0.0218 (14)
C5	0.0798 (14)	0.1023 (18)	0.0470 (10)	−0.0041 (13)	0.0163 (9)	−0.0046 (10)
C6	0.0488 (9)	0.0674 (12)	0.0609 (11)	−0.0088 (8)	0.0119 (8)	0.0019 (9)
C7	0.0876 (15)	0.0694 (15)	0.0654 (13)	−0.0281 (12)	0.0101 (10)	0.0034 (10)
C8	0.126 (3)	0.0495 (17)	0.0649 (19)	0	0.0016 (19)	0
N1	0.0413 (9)	0.0547 (12)	0.0520 (11)	0	0.0101 (8)	0
O1	0.0631 (10)	0.0560 (11)	0.0623 (11)	0	0.0133 (8)	0
O2	0.0448 (6)	0.0710 (8)	0.0430 (6)	−0.0021 (5)	0.0095 (5)	0.0021 (5)
O3	0.0360 (6)	0.0735 (8)	0.0519 (7)	0.0035 (5)	0.0069 (5)	−0.0015 (5)
V1	0.0375 (2)	0.0560 (3)	0.0412 (2)	0	0.00648 (15)	0

Geometric parameters (Å, °)

C1—O3	1.272 (2)	C6—C7	1.376 (3)
C1—C2	1.400 (2)	C6—H6	0.93
C1—C4	1.503 (2)	C7—C8	1.368 (3)
C2—C3	1.386 (2)	C7—H7	0.93
C2—H2	0.93	C8—C7^i	1.368 (3)
C3—O2	1.273 (2)	C8—H8	0.93
C3—C5	1.500 (2)	N1—C6^i	1.339 (2)
C4—H4A	0.96	N1—V1	2.422 (2)
C4—H4B	0.96	O1—V1	1.5976 (18)
C4—H4C	0.96	O2—V1	1.9918 (11)
C5—H5A	0.96	O3—V1	1.9997 (11)
C5—H5B	0.96	V1—O2^i	1.9918 (11)
C5—H5C	0.96	V1—O3^i	1.9997 (11)
C6—N1	1.339 (2)		
O3—C1—C2	124.71 (15)	C8—C7—H7	120.5
O3—C1—C4	116.22 (16)	C6—C7—H7	120.5
C2—C1—C4	119.06 (17)	C7^i—C8—C7	118.9 (3)
C3—C2—C1	125.41 (17)	C7^i—C8—H8	120.6
C3—C2—H2	117.3	C7—C8—H8	120.6
C1—C2—H2	117.3	C6—N1—C6^i	116.8 (2)
O2—C3—C2	125.04 (16)	C6—N1—V1	121.61 (11)
O2—C3—C5	115.39 (15)	C6^i—N1—V1	121.61 (11)

C2—C3—C5	119.57 (16)	C3—O2—V1	127.66 (11)
C1—C4—H4A	109.5	C1—O3—V1	127.44 (11)
C1—C4—H4B	109.5	O1—V1—O2	99.92 (4)
H4A—C4—H4B	109.5	O1—V1—O2^i	99.92 (4)
C1—C4—H4C	109.5	O2—V1—O2^i	160.16 (8)
H4A—C4—H4C	109.5	O1—V1—O3	98.30 (4)
H4B—C4—H4C	109.5	O2—V1—O3	89.55 (5)
C3—C5—H5A	109.5	O2^i—V1—O3	87.60 (5)
C3—C5—H5B	109.5	O1—V1—O3^i	98.30 (4)
H5A—C5—H5B	109.5	O2—V1—O3^i	87.60 (5)
C3—C5—H5C	109.5	O2^i—V1—O3^i	89.55 (5)
H5A—C5—H5C	109.5	O3—V1—O3^i	163.39 (8)
H5B—C5—H5C	109.5	O1—V1—N1	180
N1—C6—C7	123.16 (19)	O2—V1—N1	80.08 (4)
N1—C6—H6	118.4	O2^i—V1—N1	80.08 (4)
C7—C6—H6	118.4	O3—V1—N1	81.70 (4)
C8—C7—C6	119.0 (2)	O3^i—V1—N1	81.70 (4)
O3—C1—C2—C3	0.7 (4)	C3—O2—V1—O3^i	−166.86 (15)
C4—C1—C2—C3	−178.7 (2)	C3—O2—V1—N1	−84.87 (15)
C1—C2—C3—O2	1.0 (4)	C1—O3—V1—O1	−95.23 (15)
C1—C2—C3—C5	−179.3 (2)	C1—O3—V1—O2	4.73 (15)
N1—C6—C7—C8	−0.6 (3)	C1—O3—V1—O2^i	165.09 (15)
C6—C7—C8—C7^i	0.28 (12)	C1—O3—V1—O3^i	84.77 (15)
C7—C6—N1—C6^i	0.30 (13)	C1—O3—V1—N1	84.77 (15)
C7—C6—N1—V1	−179.70 (13)	C6—N1—V1—O2	133.93 (10)
C2—C3—O2—V1	1.2 (3)	C6^i—N1—V1—O2	−46.07 (10)
C5—C3—O2—V1	−178.52 (13)	C6—N1—V1—O2^i	−46.07 (10)
C2—C1—O3—V1	−4.3 (3)	C6^i—N1—V1—O2^i	133.93 (10)
C4—C1—O3—V1	175.11 (14)	C6—N1—V1—O3	42.93 (10)
C3—O2—V1—O1	95.13 (15)	C6^i—N1—V1—O3	−137.07 (10)
C3—O2—V1—O2^i	−84.87 (15)	C6—N1—V1—O3^i	−137.07 (10)
C3—O2—V1—O3	−3.22 (15)	C6^i—N1—V1—O3^i	42.93 (10)

Symmetry codes: (i) −x+1, y, −z+3/2.

Fig. 1

Fig. 2