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The first adduct of bis(1,3-diphenyl-1,3-propanedionato)oxovanadium(IV)

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.080
Data-to-parameter ratio = 12.8

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

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In the reaction of bis(1,3-diphenyl-1,3-propanedionato)-oxovanadium(IV) with pyridine, a 1:1 adduct is formed, *viz* bis(1,3-diphenyl-1,3-propanedionato-κ^2O,O')oxo(pyridine-κN)vanadium(IV), $[V(C_{15}H_{10}O_2)_2O(C_5H_5N)]$. The V atom is surrounded by one pyridine ligand, two 1,3-diphenyl-1,3-propandionate (dbm) ligands and one oxo group. The complex exhibits a distorted octahedral coordination, with the oxo group and pyridine ligand in a *cis* configuration. Pairs of molecules of the adduct are connected by an intermolecular C41—H41···O1($-x$, $2-y$, $1-z$) contact of 3.171 (3) Å and thus form dimers in the solid state.

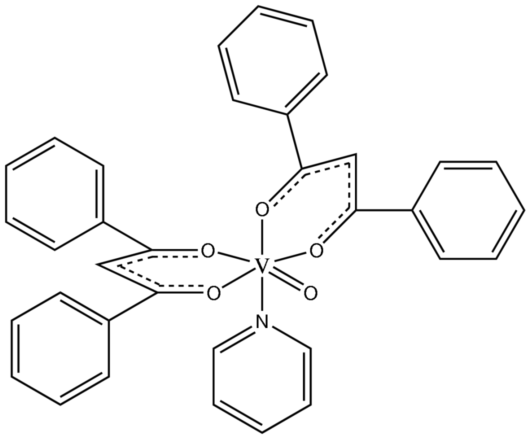
Comment

Metal and metalloid complexes with β-diketonates have been extensively studied for many years. Considerable interest has been shown in structural investigations of transition metal complexes containing pentane-1,3-dionate (acac) as a ligand; we found 1083 entries in a search of the Cambridge Structural Database (CSD, Version 5.24; Allen, 2002) for structures containing at least one acac molecular fragment. At the same time, there has been rather less interest in the structural characterization of transition metal complexes with 1,3-diphenylpropane-1,3-dionate (226 entries in CSD).

The central metal atoms in many oxygen-bonded β-diketonate complexes are coordinatively unsaturated. The completion of the coordination sphere can be achieved by bonding to another β-diketone or β-diketonate ligand, or by adduct formation with, usually, small molecules, thus acting as Lewis bases, or by polymerization.

Adducts of metal complexes are very good model systems for investigations in the area of molecular recognition and molecular association. The bonding of ligand molecules possessing various donor features to coordinatively unsaturated metal atoms in such complexes can, as a consequence, show a great variety of types of molecular association. Polymerization of either lower or higher degree is possible if the ligand has several donor sites and thus is capable of coordinating to more than one metal atom, or if it has functional groups that can participate in the formation of hydrogen bonds. The variety of spatial arrangements of ligand molecules around the metal centre (*e.g. cis* and *trans* isomerism), as well as ligand geometry, are dominating factors in the determination of the type of molecular association (Bučar & Meštrović, 2003).

Against this background, we present here the structure of the title 1:1 bis(1,3-diphenyl-1,3-propanedionato)oxovanadium(IV) pyridine adduct, (I). The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell.



(I)

The V atom in (I) is surrounded by one pyridine ligand, two 1,3-diphenyl-1,3-propanedionate (dbm) ligands and one oxo group. The complex exhibits a distorted octahedral coordination, with the oxo group and pyridine ligand in a *cis* configuration. The V atom is chelated by two dbm ligands, with bond distances given in Table 1. These values are longer than those observed for V—O$_{dbm}$ (1.941–1.957 Å) in [VO(dbm)$_2$] (Schilde *et al.*, 1995). We note that the coordination of pyridine to a coordinatively unsaturated V atom changes only the V—O$_{dbm}$ bond distances. The V═O$_{oxo}$ bond distance remains virtually unchanged compared with the value found in [VO(dbm)$_2$] (1.578 Å; Schilde *et al.*, 1995).

The chelate ring O···O separations (bite distances) are O21···O22 2.763 (2) Å and O31···O32 2.707 (2) Å, and these are significantly longer than the O···O separations between O atoms in solid Hdbm. The standard O···O distances (both O atoms are in fact involved in an intramolecular O—H···O hydrogen bond) in the structures of the three known polymorphs of non-coordinated 1,3-diphenylpropane-1,3-dione are 2.452 Å (Etter *et al.*, 1987), 2.461 Å (Kaitner & Meštrović, 1993) and 2.459 Å (Ozturk *et al.*, 1997).

Two molecules of the adduct are connected by an intermolecular C41—H41···O1($-x$, $2-y$, $1-z$) contact of 3.171 (3) Å to form dimers in the solid state.

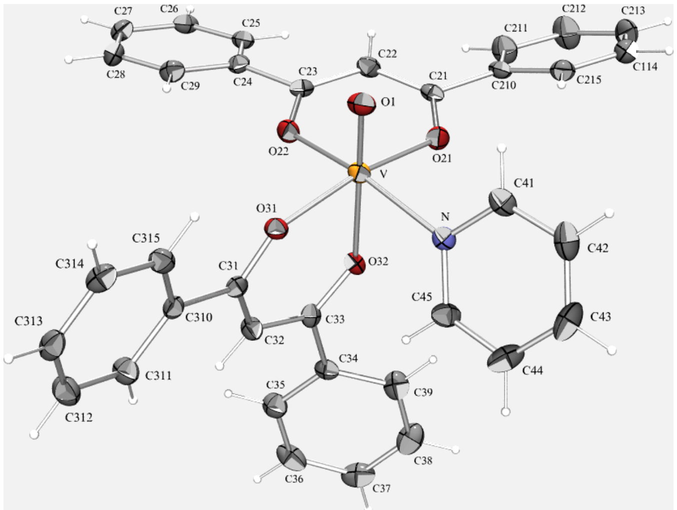


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

A mixture of V_2O_5 (1.00 g), ethanol (5.0 ml), water (2.0 ml) and sulfuric acid (2.0 ml) was refluxed for 60 min and then added to a solution of 1,3-diphenyl-1,3-propanedione (4.92 g) in ethanol (20 ml). To the resulting solution a saturated solution of sodium carbonate was added (20 ml). The resulting green precipitate of [VO(dbm)$_2$] was filtered, washed with ethanol and recrystallized from chloroform in 75% yield. [VO(dbm)$_2$] was dissolved in pyridine and left to evaporate at room temperature. After two weeks, small dark-red prismatic crystals of [VO(dbm)$_2$py] were formed.

Crystal data

$[V(C_{15}H_{10}O_2)_2O(C_5H_5N)]$
M_r = 592.52
Monoclinic, $P2_1/c$
a = 15.291 (4) Å
b = 18.973 (4) Å
c = 9.831 (2) Å
β = 97.920 (18)°
V = 2824.9 (10) Å^3
Z = 4
D_x = 1.393 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2609 reflections
θ = 2.3–14.5°
μ = 0.40 mm^{-1}
T = 100 (1) K
Prism, dark red
0.2 × 0.1 × 0.1 mm

Data collection

Oxford Xcalibur 3 CCD area-detector diffractometer
ω scans
Absorption correction: analytical (Alcock, 1970)
T_{min} = 0.867, T_{max} = 0.924
20 841 measured reflections
4865 independent reflections
3404 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 25.1°
$h = -18 \rightarrow 18$
$k = -22 \rightarrow 22$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.081
S = 0.94
4865 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

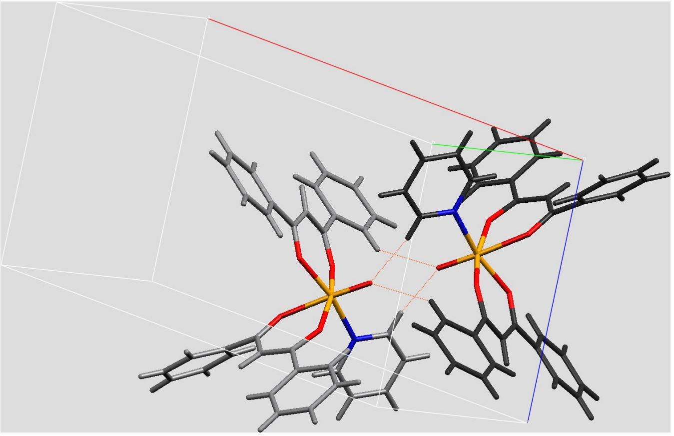


Figure 2
A plot showing the dimer of adduct (I) connected by the intermolecular C41—H41···O1($-x$, $2-y$, $1-z$) contact.

Acta Cryst. (2004). E**60**, m1920–m1922 Ernest Meštrović *et al.* • [V(C$_{15}$H$_{10}$O$_2$)$_2$O(C$_5$H$_5$N)] **m1921**

Table 1
Selected geometric parameters (Å, °).

V—O1	1.5984 (16)	V—O21	1.9858 (15)
V—O22	1.9729 (16)	V—O32	2.1427 (17)
V—O31	1.9830 (16)	V—N	2.1469 (18)
O1—V—O22	97.67 (7)	O22—V—N	87.39 (6)
O1—V—O31	95.44 (8)	O31—V—N	91.26 (7)
O22—V—O31	166.88 (7)	O21—V—N	166.93 (7)
O1—V—O21	98.62 (7)	O32—V—N	83.79 (7)
O22—V—O21	88.52 (6)	C33—O32—V	130.19 (14)
O31—V—O21	89.91 (6)	C23—O21—V	127.77 (14)
O1—V—O32	176.64 (7)	C31—O31—V	136.04 (14)
O22—V—O32	84.97 (6)	C21—O22—V	127.85 (14)
O31—V—O32	81.91 (6)	C41—N—C45	117.5 (2)
O21—V—O32	83.49 (6)	C41—N—V	118.25 (15)
O1—V—N	94.23 (8)	C45—N—V	124.17 (17)

H atoms were placed in geometric positions and treated as riding, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST*97 (Nardelli, 1995).

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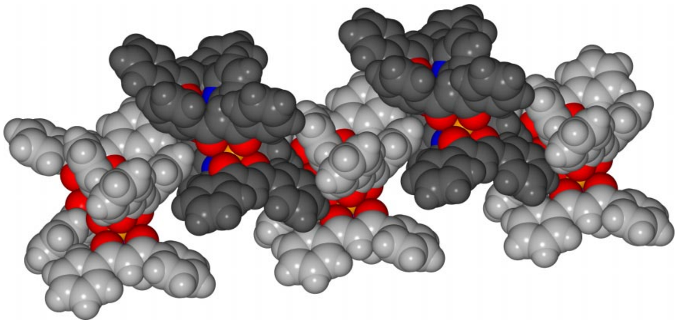

Figure 3
The crystal packing of dimers of (I) in the solid state.

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