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Methoxyoxobis(quinolin-8-olato-$\kappa^2 N,O$)vanadium(V)

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Key indicators

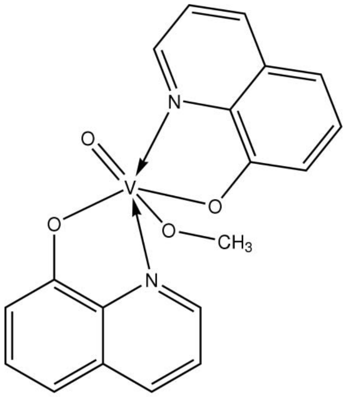
Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.116
Data-to-parameter ratio = 16.1

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

The title compound, $[V(C_9H_6NO)_2(CH_3O)O]$, crystallizes with two independent molecules in the asymmetric unit. The V^V ion is in a distorted octahedral coordination environment, with the N donors of the two chelating quinolin-8-olate ligands arranged *trans* to the oxo and methoxy groups.

Comment

Vanadium(V) complexes are widely used as oxidation catalysts (Crans *et al.*, 2004). Vanadium haloperoxidases are enzymes capable of catalyzing the oxidation of halides to hypohalous acids, and also that of sulfides to sulfoxides by hydrogen peroxide. Moreover, the active site architecture of this class of enzymes has been found to possess striking similarities with those of some acid phosphatases (Plass, 1999). Together with results from recent density functional theory studies in comparison with spectroscopic data, which indicate the prosthetic group to be a doubly protonated $[VO_2(OH)_2]^-$ vanadate group, for which structure and function are directed by its hydrogen-bonding environment (Bangesh & Plass, 2005), this has stimulated the search for structural and functional models, in particular ones that mimic the supramolecular environment of the enzyme active site (Plass, 2003; Nica *et al.*, 2005; Pohlmann *et al.*, 2005; Lippold *et al.*, 2007).



(I)

In this context, we started to explore the chemistry of mixed-ligand oxovanadium(V) complexes with 8-hydroxyquinoline (Nica *et al.*, 2007). From attempts to utilize *n*-hydroxycarbonic acid *N*-salicylidenehydrazides as co-ligands in an *in situ* reaction with ammonium metavanadate as metal precursor, the title methoxy derivative of a bis(quinolin-8-olate)oxovanadium(V) complex, (I), was obtained.

The title compound had been reported previously (Blair *et al.*, 1958), but no crystal structure was available. The chemistry

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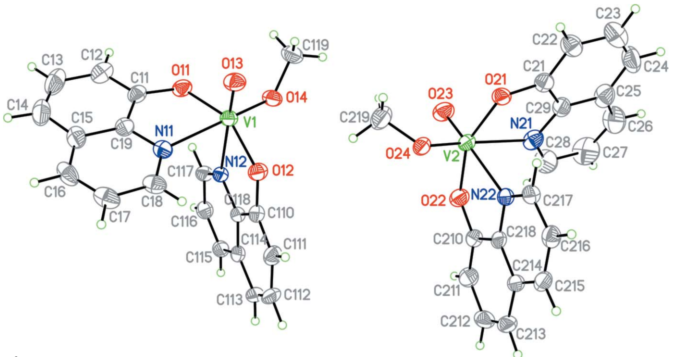

Figure 1
The structures of the two independent molecules of (I) in the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

of bis(quinolin-8-olate)vanadium(V) complexes has been explored, resulting in a series of derivatives viewed as inorganic analogues of carboxylic acids, leading to the formation of salts, esters and anhydrides, represented by dioxo- (Jeannin *et al.*, 1981; Giacomelli *et al.*, 1982; Rao *et al.*, 1998), monooxo- (Scheidt, 1973; Okabe *et al.*, 2002) and μ_2-oxo (Yamada *et al.*, 1984) derivatives.

The title compound crystallizes with two independent molecules in the asymmetric unit (Fig. 1). Each molecule contains a V^V ion in a distorted octahedral coordination environment. Two quinolin-8-olate ligands coordinate in a bidentate fashion with the positions *trans* to the two N atoms occupied by the oxo and methoxy groups, due to their structural directing effect. This leads to an overall [N_2O_4] coordination environment, with the two O donor atoms of the quinolin-8-olate groups arranged in a *trans* configuration. The bond lengths and angles (Table 1) are in the typical ranges observed for this family of complexes (Nica *et al.*, 2007; Plass & Yozgatli, 2003; Plass *et al.*, 2000). The dihedral angles between the mean planes of the two quinolin-8-olate ligands are 86.34 (4) and 89.87 (5)° for the molecules containing V1 and V2, respectively. This allows for efficient π–π stacking interactions throughout the crystal structure, with an average distance between the aromatic systems of *ca* 3.30 Å.

Experimental

To a suspension of NH_4VO_3 (0.234 g, 2 mmol) in methanol (10 ml) was added a methanol solution (30 ml) of *N*-salicylidene *n*-hydroxycarbonic acid hydrazide (2 mmol). The resulting slurry was refluxed for 2 h, after which a methanol solution (5 ml) of 8-hydroxyquinoline (0.29 g, 2 mmol) was added dropwise over a period of *ca* 15 min. The mixture was further refluxed for 1 h, followed by filtration of the hot reaction mixture to remove possible unreacted inorganic salts. The solvent was removed *in vacuo*, giving a dark-violet solid residue. Extraction of this residue with chloroform (*ca* 10 ml) afforded a dark-violet solution and an insoluble yellow solid material identified as the corresponding *cis*-dioxovanadium(V) complex with the ω-hydroxycarbonic acid *N*-salicylidenehydrazide as supporting ligand (Pohlmann *et al.*, 2005). Removal of the solvent and recrystallization from a $CHCl_3$–MeOH (1:1 *v*/*v*) solution afforded dark-purple crystals of (I) within about 2 d (yield 0.23 g, 0.6 mmol, 60%). Analysis, found: C 59.06, H 3.82, N 7.28%; calculated for $C_{19}H_{15}N_2O_4V$: C 59.08, H 3.91, N 7.25%.

Crystal data

$[V(C_9H_6NO)_2(CH_3O)O]$
$M_r = 386.27$
Monoclinic, $C2/c$
$a = 48.8807$ (13) Å
$b = 9.6542$ (2) Å
$c = 14.2788$ (4) Å
$\beta = 100.275$ (1)°
$V = 6630.2$ (3) Å^3
$Z = 16$
Mo $K\alpha$ radiation
$\mu = 0.63$ mm^{-1}
$T = 183$ (2) K
0.03 × 0.03 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: none
23067 measured reflections
7592 independent reflections
5539 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.116$
$S = 1.06$
7592 reflections
471 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.41$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V1—O13	1.5989 (17)	V2—O23	1.6031 (18)
V1—O14	1.7819 (17)	V2—O24	1.7683 (17)
V1—O12	1.8989 (17)	V2—O22	1.9017 (18)
V1—O11	1.9204 (18)	V2—O21	1.9284 (18)
V1—N11	2.201 (2)	V2—N21	2.206 (2)
V1—N12	2.301 (2)	V2—N22	2.296 (2)
O13—V1—O14	101.08 (9)	O23—V2—O24	101.74 (9)
O13—V1—O12	97.17 (8)	O23—V2—O22	95.85 (9)
O14—V1—O12	102.91 (8)	O24—V2—O22	102.20 (8)
O13—V1—O11	101.32 (8)	O23—V2—O21	101.60 (9)
O14—V1—O11	91.45 (8)	O24—V2—O21	91.82 (8)
O12—V1—O11	153.93 (8)	O22—V2—O21	154.90 (8)
O13—V1—N11	93.15 (8)	O23—V2—N21	92.72 (9)
O14—V1—N11	163.40 (8)	O24—V2—N21	163.14 (9)
O12—V1—N11	83.54 (8)	O22—V2—N21	84.68 (8)
O11—V1—N11	77.28 (8)	O21—V2—N21	76.67 (8)
O13—V1—N12	172.49 (8)	O23—V2—N22	171.10 (9)
O14—V1—N12	84.24 (7)	O24—V2—N22	84.47 (7)
O12—V1—N12	76.35 (7)	O22—V2—N22	76.46 (7)
O11—V1—N12	83.71 (7)	O21—V2—N22	84.41 (7)
N11—V1—N12	82.46 (7)	N21—V2—N22	82.21 (8)

H atoms were positioned geometrically, with C—H = 0.95 (Csp^2), 0.98 (methyl), 0.99 (methylene) or 1.00 Å (methine), and treated as riding atoms with fixed displacement parameters, $U_{\rm iso}({\rm H}) = xU_{\rm eq}({\rm C})$, where $x = 1.5$ for methyl groups and 1.2 otherwise.

Data collection: *COLLECT* (Nonius 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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