Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Aqua[*N*,*N*′-ethylenebis(salicylideneaminato-*N*,*O*)]-oxovanadium(V) nitrate 0.76-hydrate

Peter Hald, Alan Hazell,* Torben R. Jensen, Helle F. Jensen and Jens-Erik Jørgensen

Department of Chemistry, Aarhus University,
Langelandsgade 140, DK-8000 Århus C,
Denmark

Correspondence e-mail: ach@chem.au.dk

Received 8 June 2001
Accepted 14 June 2001
Online 22 June 2001

Key indicators

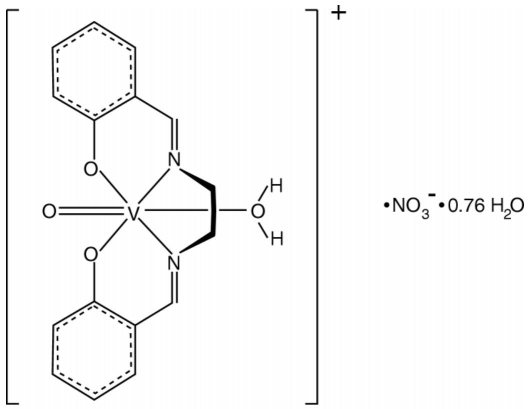
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
H-atom completeness 99%
Disorder in solvent or counterion
R factor = 0.036
wR factor = 0.040
Data-to-parameter ratio = 15.9

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

In the title compound, $[VO(C_{16}H_{16}N_2O_2)(H_2O)]NO_3\cdot0.76H_2O$, the V atom has a distorted octahedral coordination geometry with a long V—O(water) bond, 2.225 (1) Å, *trans* to V=O, 1.594 (1) Å. The V atom is 0.260 Å out of the plane defined by the N and O atoms of the bis(salicylidene)ethylenediaminate ligand and is displaced towards the vanadyl O atom. The coordinated water molecule is hydrogen bonded to one O atom of the nitrate ion so that pairs of cations are linked by two O—H···O···H—O bridges to give neutral centrosymmetric dimers. This is a different bridging arrangement from that found in either of the polymorphs of the anhydrous compound. There is also a weak hydrogen bond between a nitrate O and the partially occupied water of crystallization.

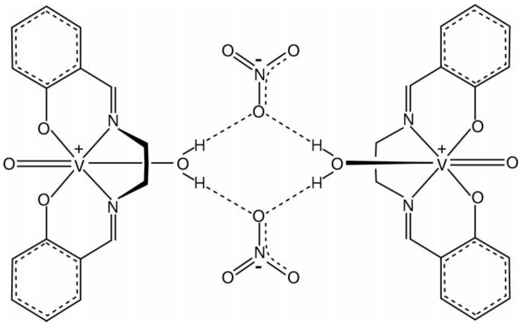
Comment

Complexes of the type V^VO(Schiff base)*Y* (*Y* = Cl, ClO_4, NO_3) can be prepared by oxidizing $V^{IV}O$(Schiff base) with $(NH_4)_2Ce(NO_3)_6$ in acetonitrile followed by the addition of HY (Nakajima *et al.*, 1990). $[V^VO(salen)(H_2O)](NO_3)$ (salen is *N*,*N*′-ethylene-bis(salicylideneaminato) prepared in this way was found to crystallize as a mixture of two polymorphs, a monoclinic, (1), and a triclinic form, (2) (Hazell *et al.*, 2001). An IR spectrum of the bulk product showed two V=O stretching frequencies, 965 and 972 cm^{-1}, corresponding to the two slightly different V=O distances in the two polymorphs. A slightly modified synthesis yielded a product that gave a single sharp V=O absorption, 974 cm^{-1}, but with cell dimensions differing from those of either of the two polymorphs. A structure determination showed the new compound to contain an extra water of crystallization.



(I)

The title compound, (I), contains $[V^VO(salen)(H_2O)]^+$ and NO_3^- ions; the cations are linked by hydrogen bonds *via* the nitrates to give neutral centrosymmetric dimers (see below and Fig. 1). The V atom is coordinated to two N and two O atoms of salen, to the vanadyl oxygen and to a water molecule which is *trans* to the vanadyl O atom; this octahedral arrangement is distorted so that the V atom is displaced out of the N_2O_2 plane in the direction of the vanadyl O atom. The displacement, 0.260 Å, is similar to that in (1), 0.255 Å, and (2), 0.260 Å, and is is slightly smaller than the value of 0.270 Å observed in the cation of $[V^VO(salen)(H_2O)]_2(Cu_2Cl_4)$, (3) (Banci *et al.*, 1984). The V═O distances in compounds (1), (2) and (3) and the title compound (I) are 1.597 (1), 1.588 (3), 1.590 (5) and 1.594 (1) Å, respectively. The V—O(water) distances are 2.257 (1), 2.230 (3), 2.310 (5) and 2.225 (1) Å, respectively, in the four compounds, which are much longer than the usual V^V—O distance, *cf.* V—O(salen) distances of 1.805–1.838 Å. The coordinated water molecules are hydrogen bonded to the nitrate ion so that there are two nitrate bridges between pairs of cations with O(nitrate)···O(water) = 2.720 (2) and 2.742 (2) Å and there is a weaker hydrogen bond, O(nitrate)···O(water) = 2.909 (4) Å to the water of crystallization. In (1) and (2), the cations are also linked by hydrogen bonds *via* the nitrates; a major difference is that here only one nitrate O atom is involved in the bridging, *i.e.* H···$O(NO_2)$···H instead of H···O(NO)O···H. The V···V distance is 8.409 (1) Å which is longer than those of 7.846 (1) Å in (1) and 7.850 (2) Å in (2). There are three different N—O bond distances, 1.265 (2) Å to the O atom involved in the strongest hydrogen bond, 1.226 (2) Å to the O atom not hydrogen bonded and 1.241 (2) Å to the O which is only weakly hydrogen bonded. The water of crystallization is disordered over two sites with occupations of 0.59 (1) for O8 and 0.17 (1) for O9. The dimers pack so that the salen groups are parallel to each other as in (1); the density is 1.582 Mg m^{-3} which is the same as that for the triclinic polymorph (1).



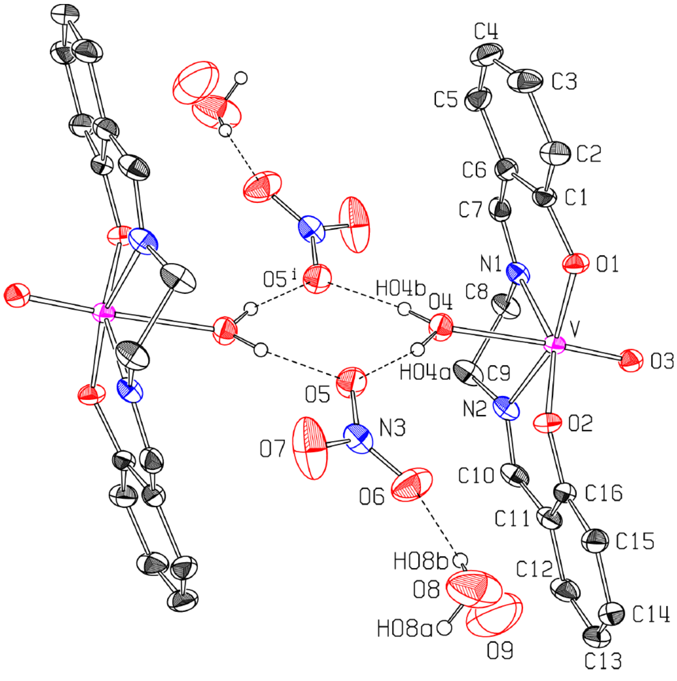


Figure 1
View of the title compound showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and the H atoms of the water molecules are shown as small circles of arbitrary radius. [Symmetry code: (i) $1 - x, 1 - y, 2 - z$.]

Experimental

4.904 g (8.945 mmol) of $(NH_4)_2Ce(NO_3)_6$ in 450 ml acetonitrile was added to 2.500 g (7.502 mmol) of $V^{IV}O(salen)$ in 375 ml acetonitrile. The volume was reduced to 250 ml by boiling on a water bath and 225 ml of 1.5 *M* nitric acid was added. After 24 h, 0.866 g (2.03 mmol) of dark-violet crystals were collected by filtration. A furthur 1.970 g (4.613 mmol) of smaller crystals precipitated during the next week. IR spectra (KBr disc, Perkin Elmer FT–IR spectrometer) ν(V═O) 974 cm^{-1} for both crops of crystals. This preparation differs from that described in Hazell *et al.* (2001), in that here the nitric acid was added directly to the solution of $V^{IV}O(salen)$ instead of to the solid.

Crystal data

$[VO(C_{16}H_{16}N_2O_2)(H_2O)]NO_3\cdot0.76H_2O$
$M_r = 426.97$
Triclinic, $P\bar{1}$
$a = 9.482$ (1) Å
$b = 9.859$ (1) Å
$c = 10.324$ (2) Å
$\alpha = 74.995$ (2)°
$\beta = 74.022$ (2)°
$\gamma = 85.559$ (3)°
$V = 896.1$ (2) Å^3

$Z = 2$
$D_x = 1.582$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9019 reflections
$\theta = 2.1$–29.7°
$\mu = 0.60$ mm^{-1}
$T = 120$ K
Block, violet
0.50 × 0.40 × 0.24 mm

Data collection

Siemens SMART CCD diffractometer
ω rotation scans with narrow frames
Absorption correction: by integration (*XPREP*; Siemens, 1995)
$T_{min} = 0.741$, $T_{max} = 0.872$
12 081 measured reflections

4646 independent reflections
4190 reflections with $I > 3\sigma(I)$
$R_{int} = 0.074$
$\theta_{max} = 29.7°$
$h = -13 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 13$

Refinement

Refinement on F
$R = 0.036$
$wR = 0.040$
$S = 0.97$
4190 reflections
264 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/\{[\sigma_{cs}(F^2) + 0.2+1.03F^2]^{1/2} - |F|\}^2$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.40$ (8) e Å^{-3}
$\Delta\rho_{min} = -0.81$ (8) e Å^{-3}

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Table 1
Selected bond lengths (Å).

V—O1	1.820 (1)	V—O4	2.225 (1)
V—O2	1.831 (1)	V—N1	2.090 (2)
V—O3	1.594 (1)	V—N2	2.076 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—HO4$a\cdots$O5	0.86	1.88	2.720 (2)	168
O4—HO4$b\cdots$O5^{i}	0.86	1.89	2.742 (2)	172
O8—HO8$b\cdots$O6	0.86	2.07	2.909 (4)	168

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

The H atoms of the ligand were constrained to have C—H = 0.95 Å and $U_{\rm iso} = 1.2U_{\rm eq}$ for the atom to which they are attached. The H atoms of the water molecules O4 and O8 were obtained from a difference map and kept fixed. It was only after O9 (which is only 1 Å from O8) was included in the refinement that the H atoms on O8 could be located. Those of O9 were neither located or included in the refinement.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997) and *KRYSTAL* (Hazell, 1995); program(s) used to refine structure: modified *ORFLS* (Busing *et al.*, 1962) and *KRYSTAL*; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

We are indebted to the Carslberg Foundation for the diffractometer and for the cooling device.

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