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Two polymorphs of aqua[*N*,*N*′-ethylenebis(salicylideneaminato-*N*,*O*)]-oxovanadium(V) nitrate

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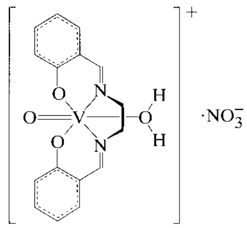
The title compound, aqua[bis(salicylidene)ethylenediaminato-*O*,*N*,*N*′,*O*′]oxovanadium(V) nitrate, $[VO(C_{16}H_{14}N_2O_2)(H_2O)]NO_3$, crystallizes as two polymorphs in the triclinic and monoclinic crystal systems. In both, the V atom has a distorted octahedral coordination geometry with a long V—O_{water} bond *trans* to V═O. The coordinated water molecules are hydrogen bonded to the nitrate ions so that pairs of cations are linked to give neutral centrosymmetric dimers. The V═O and V—O_{water} distances are 1.598 (2) and 2.257 (2) Å, respectively, in the triclinic form, and 1.588 (3) and 2.230 (3) Å, respectively, in the monoclinic form. In the triclinic form, the dimers pack so that the salen [bis(salicylidene)ethylenediaminate] ligands are parallel to each other, whereas in the monoclinic form, which is the denser, there is a herring-bone arrangement.

Comment

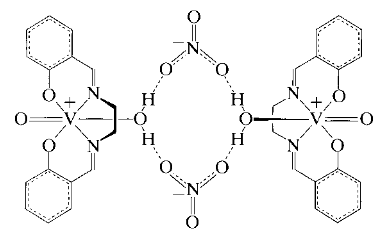
Complexes of the type $[V^VO(\text{Schiff base})]Y$ (*Y* is Cl, ClO_4 or NO_3) can be prepared by oxidizing $[V^{IV}O(\text{Schiff base})]$ with $(NH_4)_2Ce(NO_3)_6$ in acetonitrile, followed by the addition of H*Y* (Nakajima *et al.*, 1990). The structure of $[V^VO(\text{salen})]ClO_4$ [salen is *N*,*N*′-bis(salicylidene)ethylenediaminate] has been studied by X-ray diffraction by Bonadies *et al.* (1987) and the V atom shown to have a distorted octahedral coordination, with a long [2.456 (3) Å] V—$O_{perchlorate}$ bond *trans* to V═O. Nakajima *et al.* (1990) proposed, on the basis of absorption



(I), (II)

spectra, that their $[V^VO(\text{Schiff base})]Y$ complexes had structures analogous to that of the $[V^VO(\text{salen})]ClO_4$ complex. A structural investigation of $[V^VO(\text{salen})]NO_3$ prepared by Nakajima's method showed the product to contain two polymorphs, a triclinic form, (I), and a monoclinic form, (II), which contain $[V^VO(\text{salen})(H_2O)]^+$ and NO_3^- ions. The structures of these two polymorphs are presented here.

In both forms, the cations are linked by hydrogen bonds *via* the nitrates to give centrosymmetric dimers (see scheme below; Figs. 1 and 2). The V atoms are coordinated to two N atoms and two O atoms of the salen ligand, to the vanadyl oxygen, and to a water molecule, which is *trans* to the V═O oxygen. This octahedral arrangement is distorted, in that the V atom is displaced out of the N_2O_2 plane in the direction of the vanadyl oxygen by 0.255 Å in (I) and 0.260 Å in (II), which is similar to the value of 0.270 Å observed in the cation of $[V^VO(\text{salen})\text{-}(H_2O)]_2[Cu_2Cl_4]$, (III) (Banci *et al.*, 1984). The V═O distances in compounds (I), (II) and (III) are 1.598 (2), 1.588 (3) and 1.590 (5) Å, respectively, and the V—O_{water} distances are 2.257 (2), 2.230 (3) and 2.310 (5) Å, respectively.



These latter values are much longer than the usual V^V—O distance; *cf.* V—O_{salen} of 1.823 (2) and 1.838 (2) Å in (I), and 1.835 (3) and 1.805 (3) Å in (II). An indication that the V═O distances in (I) and (II) really are different is that the V═O absorption in the IR spectrum of the bulk sample is a doublet.

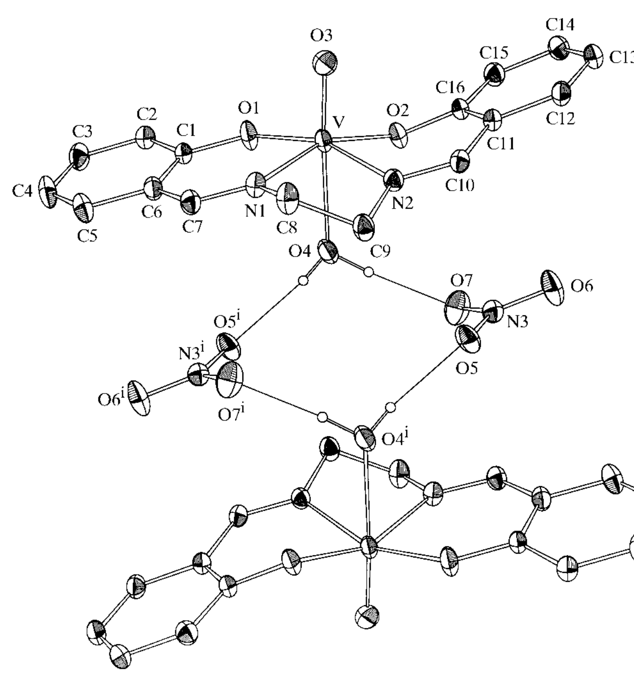


Figure 1
A view of the $\{[V^VO(\text{salen})(H_2O)]NO_3\}_2$ dimer in (I) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms of the water molecules are shown as small circles of arbitrary radii; other H atoms have been omitted for clarity [symmetry code: (i) $1-x, -y, 1-z$].

The water molecules are hydrogen bonded to the nitrate ion so that there are two nitrate bridges between pairs of cations; $O_{water}\cdots O_{nitrate}$ distances are 2.737 (2) and 2.779 (2) Å in (I), and 2.705 (4) and 2.813 (4) Å in (II). The V···V distance in the dimers is almost identical; 7.846 (1) Å in (I) and 7.850 (2) Å in (II). In both cases, the N—O bond for the non-hydrogen-bonded O atom is the shortest; 1.240 (2) Å in (I) and 1.243 (4) Å in (II), compared with 1.260 (2) and 1.263 (2) Å for the remaining two N—O bonds in (I), and 1.254 (4) and 1.258 (4) Å for the remaining two N—O bonds in (II).

Packing diagrams have been deposited. In the triclinic form, (I), the dimers pack so that the salen groups are parallel to each other, whereas in the monoclinic form, (II), there is a herring-bone arrangement, with an angle of 50° between the planes through the salen ligands. The monoclinic form, (II), is the denser, with ρ = 1.609, *cf.* 1.582 for (I).

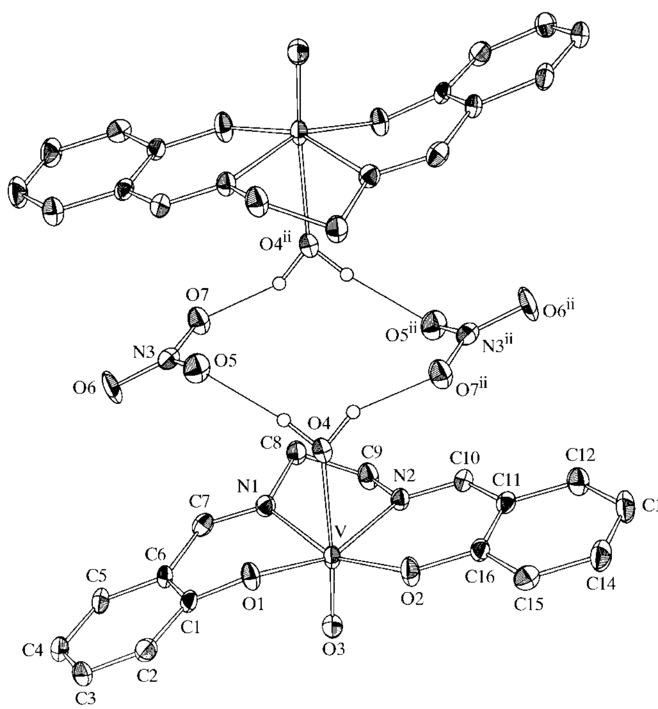


Figure 2
A view of the $\{[V^{V}O(salen)(H_2O)]NO_3\}_2$ dimer in (II) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms of the water molecules are shown as small circles of arbitrary radii; other H atoms have been omitted for clarity [symmetry code: (ii) $\frac{3}{2}-x, \frac{1}{2}-y, -z$].

Experimental

$(NH_4)_2Ce(NO_3)_6$ (2.0 g, 3.6 mmol) in acetonitrile (180 ml) was added to $V^{IV}O$(salen) (1.0 g, 3 mmol) in acetonitrile (90 ml). The volume was reduced to 90 ml using a rotary evaporator. The crude product was filtered and then dissolved in 1.5 *M* nitric acid (90 ml), from which dark-violet crystals of the two polymorphs, (I) and (II), were obtained after 24 h (yield 0.7 g, 1.7 mmol). IR spectra (KBr): ν(V=O) 965, 972 cm^{-1}.

Compound (I)

Crystal data

$[VO(C_{16}H_{14}N_2O_2)(H_2O)]NO_3$
M_r = 413.28
Triclinic, $P\overline{1}$
a = 8.663 (2) Å
b = 8.956 (2) Å
c = 13.293 (3) Å
α = 73.029 (3)°
β = 83.852 (4)°
γ = 61.662 (3)°
V = 867.7 (3) Å^3
Z = 2
D_x = 1.582 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4080 reflections
θ = 2.7–29.8°
μ = 0.618 mm^{-1}
T = 120 K
Plate, dark violet
0.40 × 0.23 × 0.10 mm

Data collection

Siemens SMART CCD diffractometer
ω rotation scans
Absorption correction: by integration (*XPREP*; Siemens, 1995)
T_{min} = 0.765, T_{max} = 0.943
16 803 measured reflections
4960 independent reflections
3763 reflections with $I > 3\sigma(I)$
R_{int} = 0.082
θ_{max} = 29.8°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 19$

Refinement

Refinement on F
R = 0.033
wR = 0.042
S = 1.327
3763 reflections
252 parameters
H atoms treated by a mixture of independent and constrained refinement
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.49 (7) e Å^{-3}
$\Delta\rho_{min}$ = −0.52 (7) e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

V—O1	1.823 (2)	V—O4	2.257 (2)
V—O2	1.838 (2)	V—N1	2.106 (2)
V—O3	1.598 (2)	V—N2	2.093 (2)
O1—V—N2	159.04 (6)	O3—V—O4	172.02 (6)
O2—V—N1	157.18 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—HO4*a*···O7	0.89 (2)	1.89 (3)	2.779 (2)	175 (2)
O4—HO4*b*···O5^{i}	0.79 (3)	1.97 (3)	2.737 (2)	168 (3)

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

Compound (II)

Crystal data

$[VO(C_{16}H_{14}N_2O_2)(H_2O)]NO_3$
M_r = 413.28
Monoclinic, $C2/c$
a = 16.413 (2) Å
b = 8.1634 (8) Å
c = 25.628 (3) Å
β = 96.619 (2)°
V = 3411.1 (6) Å^3
Z = 8
D_x = 1.609 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2493 reflections
θ = 1.6–29.8°
μ = 0.628 mm^{-1}
T = 120 K
Plate, dark violet
0.41 × 0.19 × 0.12 mm

Data collection

Siemens SMART CCD diffractometer	4831 independent reflections
ω rotation scans	2461 reflections with $I > 2\sigma(I)$
Absorption correction: by integration (*XPREP*; Siemens, 1995)	$R_{int} = 0.135$
$T_{min} = 0.820$, $T_{max} = 0.992$	$\theta_{max} = 29.8°$
19 982 measured reflections	$h = -22 \rightarrow 22$
	$k = -11 \rightarrow 11$
	$l = -35 \rightarrow 35$

Refinement

Refinement on F	244 parameters
$R = 0.050$	H atoms parameters constrained
$wR = 0.047$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.059$	$\Delta\rho_{max} = 0.33$ (5) e Å^{-3}
2461 reflections	$\Delta\rho_{min} = -0.39$ (5) e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

V—O1	1.835 (3)	V—O4	2.230 (3)
V—O2	1.805 (3)	V—N1	2.066 (3)
V—O3	1.588 (3)	V—N2	2.089 (3)
O1—V—N2	157.7 (1)	O3—V—O4	172.8 (1)
O2—V—N1	158.4 (1)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—HO4*b*···O7^{ii}	0.92	1.88	2.705 (4)	150
O4—HO4*a*···O5	0.91	1.91	2.813 (4)	172

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

The H atoms of the water molecules were obtained from a difference map. For (I), these coordinates and an isotropic displacement parameter were refined; for (II), the H-atom coordinates were kept fixed at the observed positions. For both structures, the H atoms of the ligand were constrained to have C—H = 0.95 Å and $U_{iso} = 1.2U_{eq}$ of the parent atom. The weighting scheme employed was $w = 1/[\sigma_{cs}(F)]^2$, where $\sigma_{cs}(F) = [\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|$, *i.e* $\sigma_{cs}(F) = \sigma_{cs}(F^2)/2F$ for large F and small $\sigma_{cs}(F^2)$, and $\sigma_{cs}(F) = [\sigma_{cs}(F^2)]^{1/2}$ for small F^2.

For both compounds, 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1035). Services for accessing these data are described at the back of the journal.

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