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## Monooxovanadium(V) complexes with bidentate *N*-phenylbenzohydroxamate

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### Abstract

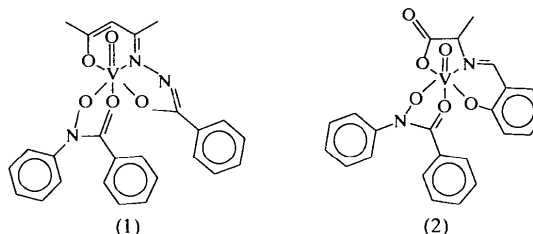
Two complexes of oxovanadium(V) with VO(ONO)-(OO)-type coordination were synthesized and analysed by X-ray diffraction. These compounds are (acetylacetonone benzoylhydrazonato-*O,N,O'*)(*N*-hydroxy-*N*-phenylbenzamido-*O,O'*)oxovanadium(V), [VO(C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>)(C<sub>13</sub>H<sub>10</sub>NO<sub>2</sub>)], and (*N*-hydroxy-*N*-phenylbenzamido-*O,O'*)oxo(*N*-salicylidene-*L*-alaninato-*O,N,O'*)vanadium(V), [VO(C<sub>10</sub>H<sub>9</sub>NO<sub>3</sub>)(C<sub>13</sub>H<sub>10</sub>NO<sub>2</sub>)]; *N*-hydroxy-*N*-phenylbenzamide is also known as *N*-phenylbenzohydroxamic acid. The distorted octahedral coordination at vanadium is similar in both complexes; the equatorial plane is defined by one N and two O atoms of the tridentate hydrazone ligand and the oxime O atom of the hydroxamate ligand, while the axial oxo group is *trans* to the carbonyl O atom of the hydroxamate ligand.

### Comment

The presence of hydroxamic acids at the active sites of some biological enzymes (Kurzak *et al.*, 1992) and the discovery of the biological relevance of hydroxamate–vanadium complexes (Cornman *et al.*, 1992) have resulted in increased interest in the study of their structural properties. However, only a few structures of the simplest vanadium complexes with hydroxamate ligands have been reported (Cornman *et al.*, 1992; Fisher *et al.*, 1989; Pecoraro, 1989; Gibney *et al.*, 1993; Liu & Gao, 1998, 1999).

As part of a continuing study of oxovanadium–hydroxamate complexes, we report the syntheses and structures of (acetylacetonone benzoylhydrazonato-*O,N,O'*)oxo(*N*-phenylbenzohydroxamate-*O,O'*)vanadium(V), (1), and oxo(*N*-phenylbenzohydroxamate-*O,O'*)(*N*-salicylidene-*L*-alaninato-*O,N,O'*)vanadium(V), (2). The coordination geometry and bond parameters of

(1) and (2) are similar to those in [VOL<sup>1</sup>(bbz)] and [VOL<sup>2</sup>(bbz)]·CH<sub>3</sub>OH [where H<sub>2</sub>L<sup>1</sup> is *N*-salicylidene-glycine, H<sub>2</sub>L<sup>2</sup> is *N*-(2-carboxyphenyl)salicylideneamine and H<sub>2</sub>bbz is *N*-phenylbenzohydroxamic acid; Liu & Gao, 1999].



In both compounds, the atom *trans* to the oxo O atom is the carbonyl O atom of the hydroxamate ligand. The *trans* axial angle is 167.05 (8)<sup>o</sup> in complex (1), and 171.6 (2) and 173.6 (2)<sup>o</sup> in complex (2). The axial V—O bonds (*trans* to V=O) are longer than the equatorial V—O bonds due to the structural *trans* effect. The oxo–vanadium bond lengths range from 1.573 (3) to 1.589 (3) Å, which are within the range of most V—O bond distances.

Compound (2) crystallizes in the polar space group *P*2<sub>1</sub> with two molecules in the asymmetric unit. This is similar to its chiral precursor, aquaoxo(*N*-salicylidene-*L*-alaninato)vanadium [(IV); Hämmäläinen *et al.*, 1985]. The preparation of the complex does not influence the stereochemistry at the chiral C8 and C8' atoms. Although the two independent molecules appear to be related by a centre of inversion, as would occur if the space group were *P*2<sub>1</sub>/*n*, refinement in this centrosymmetric space group would not converge. Careful examination of the stereochemistry at the chiral C atoms shows that both chiral centres (C8 and C8') have the

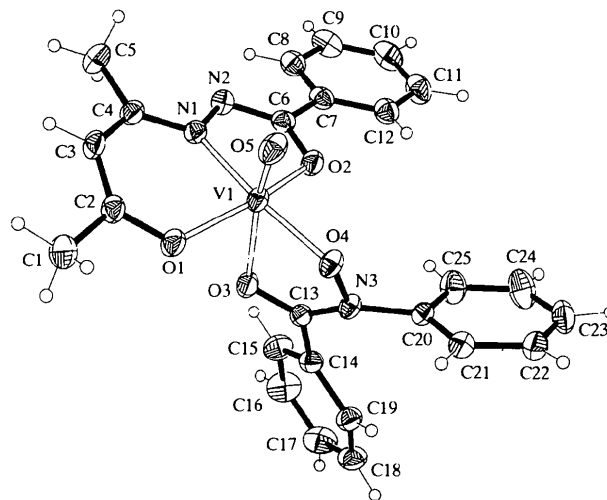


Fig. 1. ORTEP (Johnson, 1976) plot for (1) drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii.

same handedness. The lack of inversion symmetry is evident from the torsion angles O2—C9—C8—N1 versus O2'—C9'—C8'—N1' [−9.9(6) and 21.2(6)°, respectively] and O3—C9—C8—C10 versus O3'—C9'—C8'—C10' [−68.7(8) and −31.9(9)°, respectively]. The centrosymmetric space group is also excluded by violations of the systematic absences for an *n*-glide plane.

The V atoms in the two independent molecules in compound (2) deviate from the least-squares plane passing through the four atoms in the equatorial plane by 0.273(2) and 0.261(2) Å towards the oxo O atom. This difference of about 0.012 Å is reflected in the difference in the axial bond distances of 1.573 and 2.177 Å in one

molecule, and of 1.589 and 2.165 Å in the other molecule.

## Experimental

Benzoylhydrazine (1 mmol) dissolved in methanol (15 ml) was added dropwise to a methanol solution (10 ml) containing VO(acac)<sub>2</sub> (1 mmol; where acac is acetylacetonate) with stirring. The mixture was refluxed for 2 h, resulting in a brown-red solution. A methanol solution (10 ml) containing *N*-phenylbenzohydroxamic acid (1 mmol) was added slowly to the above brown-red solution with stirring, and the precipitated crystals were filtered off and dried. The deep-red crystals of complex (1) were recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and collected under vacuum over P<sub>4</sub>O<sub>10</sub>. For the preparation of (2), *N*-phenylbenzohydroxamic acid (1 mmol) dissolved in methanol (10 ml) was added dropwise to a methanol solution containing [VO(*N*-salicylidene-*L*-alanine)(H<sub>2</sub>O)] (1 mmol; Theriot *et al.*, 1969). The resulting solution was stirred for 30 min, cooled and filtered. Deep-red crystals of complex (2) formed upon slow evaporation of the filtrate for several days and were collected under vacuum over P<sub>4</sub>O<sub>10</sub>.

## Compound (1)

### Crystal data

[VO(C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>)-  
(C<sub>13</sub>H<sub>10</sub>NO<sub>2</sub>)]

*M<sub>r</sub>* = 495.40

Monoclinic

*P*2<sub>1</sub>/*n*

*a* = 13.003(1) Å

*b* = 8.8836(6) Å

*c* = 20.196(2) Å

β = 95.065(8)°

*V* = 2323.8(3) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.416 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 13–14°

μ = 0.469 mm<sup>-1</sup>

*T* = 300(2) K

Irregular block

0.43 × 0.36 × 0.36 mm

Red-black

### Data collection

Enraf-Nonius CAD-4 diffractometer

ω scans

Absorption correction:

ψ scan (North *et al.*, 1968)

*T<sub>min</sub>* = 0.735, *T<sub>max</sub>* = 0.845

7029 measured reflections

6759 independent reflections

3907 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.031

θ<sub>max</sub> = 29.99°

*h* = −18 → 18

*k* = 0 → 12

*l* = 0 → 28

3 standard reflections

frequency: 60 min

intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.056

*wR*(*F*<sup>2</sup>) = 0.124

*S* = 0.976

6759 reflections

395 parameters

All H atoms refined

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0557*P*)<sup>2</sup>]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.358 e Å<sup>-3</sup>

Δρ<sub>min</sub> = −0.225 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

*International Tables for*

*Crystallography* (Vol. C)

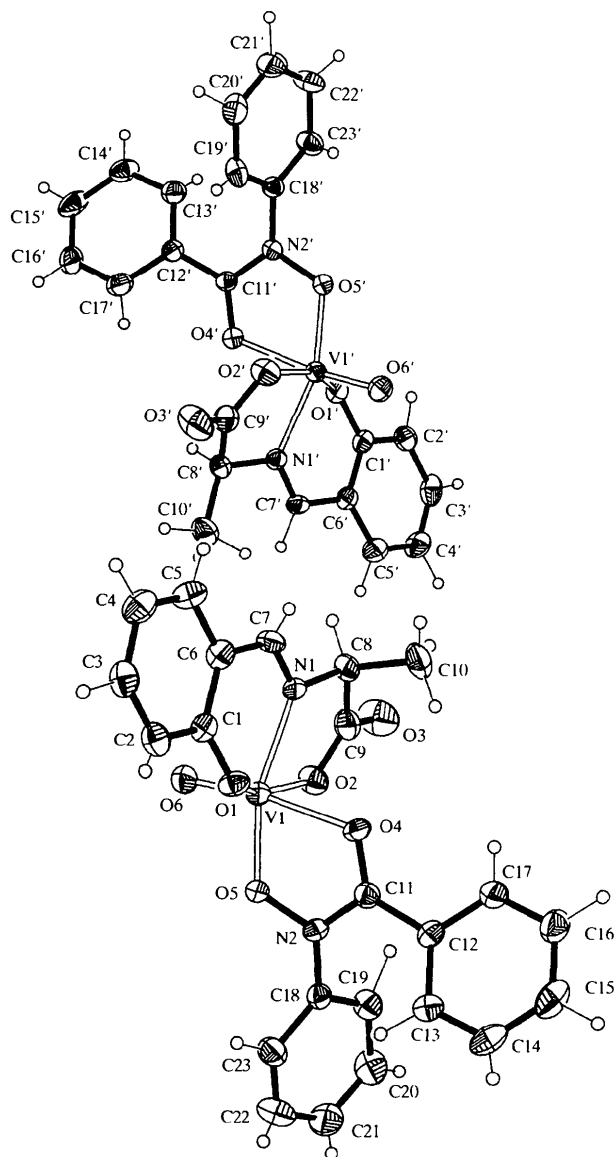


Fig. 2. ORTEP (Johnson, 1976) plot for (2) drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii.

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (1)

V1—O5	1.585 (2)	V1—O2	1.928 (2)	O1—V1—O5	104.2 (2)	O5'—V1'—O1'	104.9 (2)
V1—O4	1.864 (2)	V1—N1	2.042 (2)	O6—V1—O2	99.5 (2)	O6'—V1'—O2'	98.3 (2)
V1—O1	1.876 (2)	V1—O3	2.242 (2)	O1—V1—O2	155.9 (2)	O5'—V1'—O2'	90.0 (2)
O5—V1—O4	94.77 (8)	O1—V1—N1	85.17 (7)	O5—V1—O2	90.3 (2)	O1'—V1'—O2'	157.7 (2)
O5—V1—O1	97.46 (9)	O2—V1—N1	75.33 (7)	O6—V1—N1	99.4 (2)	O6'—V1'—N1'	99.8 (2)
O4—V1—O1	107.62 (7)	O5—V1—O3	167.05 (8)	O1—V1—N1	83.8 (2)	O5'—V1'—N1'	159.69 (15)
O5—V1—O2	106.22 (9)	O4—V1—O3	73.94 (6)	O5—V1—N1	161.05 (15)	O1'—V1'—N1'	83.6 (2)
O4—V1—O2	87.44 (7)	O1—V1—O3	80.41 (7)	O2—V1—N1	77.0 (2)	O2'—V1'—N1'	77.2 (2)
O1—V1—O2	150.82 (8)	O2—V1—O3	80.06 (7)	O6—V1—O4	171.6 (2)	O6'—V1'—O4'	173.6 (2)
O5—V1—N1	97.18 (8)	N1—V1—O3	95.37 (7)	O1—V1—O4	80.9 (2)	O5'—V1'—O4'	76.02 (14)
O4—V1—N1	161.20 (7)			O5—V1—O4	75.79 (13)	O1'—V1'—O4'	84.74 (14)
				O2—V1—O4	84.2 (2)	O2'—V1'—O4'	82.9 (2)
				N1—V1—O4	88.82 (14)	N1'—V1'—O4'	86.69 (14)

**Compound (2)***Crystal data*[VO(C<sub>10</sub>H<sub>9</sub>NO<sub>3</sub>)-  
(C<sub>13</sub>H<sub>10</sub>NO<sub>2</sub>)] $M_r = 470.34$ 

Monoclinic

 $P2_1$  $a = 9.720 (1) \text{\AA}$  $b = 18.274 (2) \text{\AA}$  $c = 12.542 (1) \text{\AA}$  $\beta = 104.868 (9)^\circ$  $V = 2153.2 (4) \text{\AA}^3$  $Z = 4$  $D_r = 1.451 \text{ Mg m}^{-3}$  $D_m$  not measured*Data collection*Enraf–Nonius CAD-4  
diffractometer $\omega$  scans

Absorption correction:

 $\psi$  scan (North *et al.*,  
1968) $T_{\min} = 0.877$ ,  $T_{\max} = 0.932$ 

10 297 measured reflections

9867 independent reflections

*Refinement*Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.062$  $wR(F^2) = 0.145$  $S = 0.970$ 

9867 reflections

729 parameters

All H atoms refined

 $w = 1/[\sigma^2(F_o^2) + (0.0745P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = -0.001$ Mo  $K\alpha$  radiation $\lambda = 0.71073 \text{\AA}$ 

Cell parameters from 25

reflections

 $\theta = 11\text{--}12^\circ$  $\mu = 0.504 \text{ mm}^{-1}$  $T = 300 (2) \text{ K}$ 

Wedge

 $0.32 \times 0.28 \times 0.14 \text{ mm}$ 

Red–black

6562 reflections with

 $I > 2\sigma(I)$  $R_{\text{int}} = 0.048$  $\theta_{\max} = 27.48^\circ$  $h = -12 \rightarrow 12$  $k = -23 \rightarrow 23$  $l = 0 \rightarrow 16$ 

3 standard reflections

frequency: 60 min

intensity decay: 6%

 $\Delta\rho_{\max} = 0.360 \text{ e \AA}^{-3}$  $\Delta\rho_{\min} = -0.395 \text{ e \AA}^{-3}$ 

Extinction correction: none

Scattering factors from

*International Tables for  
Crystallography* (Vol. C)

Absolute structure:

Flack (1983)

Flack parameter = 0.00 (3)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (2)

V1—O6	1.573 (3)	V1'—O6'	1.589 (3)
V1—O1	1.859 (4)	V1'—O5'	1.860 (4)
V1—O5	1.862 (3)	V1'—O1'	1.872 (4)
V1—O2	1.928 (4)	V1'—O2'	1.949 (4)
V1—N1	2.081 (4)	V1'—N1'	2.062 (4)
V1—O4	2.177 (3)	V1'—O4'	2.165 (3)
O6—V1—O1	97.9 (2)	O6'—V1'—O5'	97.6 (2)
O6—V1—O5	96.5 (2)	O6'—V1'—O1'	96.1 (2)

All H atoms in complex (1) were located from a difference map, while six H atoms from complex (2) could not be located and were generated geometrically. All H atoms were refined isotropically.

For both compounds, data collection: *CAD-4 VAX/PC* (Enraf–Nonius, 1988); cell refinement: *CAD-4 VAX/PC*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990a); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1036). Services for accessing these data are described at the back of the journal.

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