

Zhao-Peng Deng, Shan Gao,*
Li-Hua Huo and Hui ZhaoLaboratory of Functional Materials, School of
Chemistry and Materials Science, Heilongjiang
University, Harbin 150080, People's Republic
of ChinaCorrespondence e-mail:
shangao67@yahoo.com

Key indicators

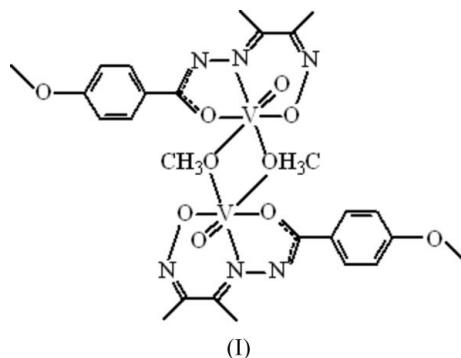
Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.041
 wR factor = 0.117
Data-to-parameter ratio = 17.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Di- μ -methoxy-bis[[diacetyl monoxime (4-methoxy-
benzoyl)hydrazonato- $\kappa^3\text{O},\text{N},\text{N}'$]oxovanadium(V)]

In the title centrosymmetric dimeric complex, $[\text{V}_2(\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_3)_2(\text{CH}_3\text{O})_2\text{O}_2]$, each V^{V} atom is six-coordinated by one oxo O atom, two N atoms and one O atom of the tridentate hydrazone ligand and two O atoms of two methoxy groups, leading to a distorted octahedral environment. Two V^{V} atoms are bridged by methoxy groups, resulting in a dimer, with a $\text{V}\cdots\text{V}$ separation of 3.324 (3) Å.

Received 26 September 2005
Accepted 30 September 2005
Online 8 October 2005

Comment

In the past few decades, there has been increased interest in the coordination chemistry and biochemistry of oxovanadium because of the possible function of vanadium in several biological processes (Crans *et al.*, 1997; Butler & Walker, 1993; Rehder, 1991), such as a cofactor in haloperoxidases and nitrogenases (Martinez *et al.*, 2001). Generally, a tridentate hydrazone ligand is coordinated to the vanadium through O and N atoms, similar to those of the biological system. Therefore, it is important to study in detail the relationship of syntheses and structure of vanadium hydrazone complexes.



We have previously reported the structures of some oxovanadium(V) (VO^{3+}) complexes containing tridentate hydrazone ligands, in which the hydrazone ligands are formed by condensing arylhydrazines with β -diketones, salicylaldehyde and their derivatives (Gao *et al.*, 2004; Huo, Gao, Liu, Li *et al.*, 2004; Huo, Gao, Liu, Zhao *et al.*, 2004). However, less attention has been directed towards the hydrazone ligands formed by diacetyl monoxime. Recently, we have obtained a novel dimeric oxovanadium(V) complex, $[\text{VOL}(\text{CH}_3\text{O})]_2$ [L^{2-} is diacetyl monoxime (4-methoxybenzoyl)hydrazonate], (I), which was prepared by the reaction of diacetyl monoxime (4-methoxybenzoyl)hydrazone and $\text{VO}(\text{acetylacetonate})_2$ in methanol solution. As part of a continuing study of oxovanadium-hydrazone complexes, the synthesis and structure of the title complex, (I), is reported here.

The local coordination around the V^{V} atom, together with the atom-numbering scheme of (I), is illustrated in Fig. 1. The

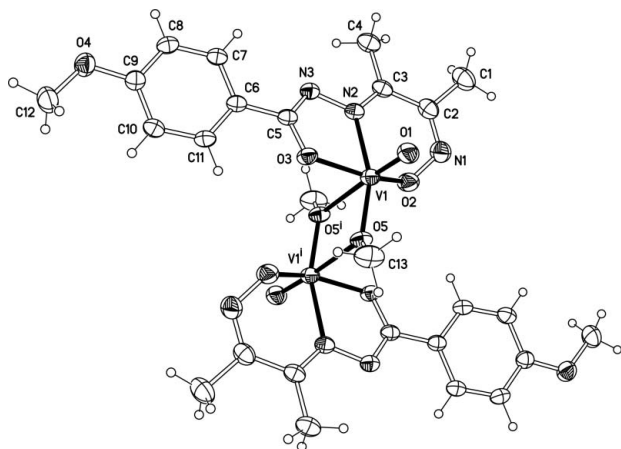


Figure 1
ORTEP (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $1 - x, 1 - y, -z$.]

dimer, which lies on a crystallographic center of symmetry, is formed by two bridging methoxide O atoms, with V1—O5 and V1—O5ⁱ [symmetry code: (i) $1 - x, 1 - y, -z$] bond lengths of 1.8386 (15) and 2.3046 (15) Å, respectively. The V···V separation is 3.324 (3) Å, and the angle V1—O5—V1ⁱ is 106.14 (7)°. Each V^V atom is six-coordinated by one O atom of the oxo group, two N atoms and one O atom of the tridentate hydrazone ligand and two O atoms of two methoxide groups, and the local coordination sphere around the V^V ion can be described as distorted octahedral with a VO₄N₂ geometry. The equatorial plane is defined by atoms O2, O3 and N2 of the fully deprotonated tridentate hydrazone ligand and atom O5 of methoxide [r.m.s. deviation = 0.0426 (8) Å; deviation of the V^V atom from this plane is 0.3198 (8) Å]. The axial oxo atom O1 is in a *trans* position relative to atom O5ⁱ of another methoxide, with an O1—V1—O5ⁱ angle of 176.15 (7)°. The V1—O1 bond distance of 1.5846 (17) Å is within the normal range in the structures of VO³⁺ complexes (Chen *et al.*, 1999). The axial V1—O5ⁱ distance of 2.3046 (15) Å is longer than the other equatorial V—O and V—N bond lengths, owing to the strong *trans* influence of the oxo group.

The tridentate hydrazone ligand combines with the V^V atom to give one five-membered and one six-membered chelate rings. The five-membered chelate ring, O3/C5/N3/N2/V1, is planar, with a mean deviation of 0.0295 (8) Å, whereas the six-membered chelate ring, N2/C3/C2/N1/O2/V1, is non-planar, with the atom V1 deviating from the N2/C3/C2/N1/O2 plane by 0.785 (3) Å. The hydrazone ligand in the title complex is approximately planar.

It can be seen from Table 1 that the lengths of the N1—C2, N2—C3, N3—C5 and O3—C5 bonds are intermediate between single- and double-bond lengths, indicating electron delocalization in the hydrazone ligand, which makes atom N2 easily deprotonated. The two methyl groups of the diacetyl monoxime group in the free hydrazone ligand lie in *trans* positions (Gao *et al.*, 2005); however, it becomes *cis* in the title complex, which can be attributed to the coordination environment of the vanadium ion and the coordination mode of the hydrazone ligand.

Experimental

The VO(acac)₂ starting material (acac[−] = acetylacetonate) was synthesized according to the method of Rowe & Jones (1957). The ligand (H₂L), diacetyl monoxime (4-methoxybenzoyl)hydrazone, was synthesized by condensing diacetyl monoxime with an equimolar quantity of (4-methoxybenzoyl)hydrazine in ethanol. The title compound was prepared by the addition of VO(acac)₂ (5 mmol) to a methanol solution (35 ml) of diacetyl monoxime (4-methoxybenzoyl)hydrazone (5 mmol). The mixture was refluxed and stirred for 1.5 h, cooled slowly to room temperature and then filtered. Black crystals were isolated from the filtered solution after several days. Analysis calculated for C₂₆H₃₂O₁₀N₆V₂: C 45.23, H 4.67, N 12.17%; found: C 45.19, H 4.64, N 12.15%.

Crystal data

[V₂(C₁₂H₁₃N₃O₃)₂(CH₃O)₂O₂]
M_r = 690.46
Monoclinic, P2₁/c
a = 7.3381 (15) Å
b = 22.166 (4) Å
c = 9.6540 (19) Å
β = 99.75 (3)°
V = 1547.6 (5) Å³
Z = 2

D_x = 1.482 Mg m^{−3}
Mo Kα radiation
Cell parameters from 13756 reflections
θ = 3.4–27.5°
μ = 0.67 mm^{−1}
T = 295 (2) K
Prism, black
0.35 × 0.23 × 0.18 mm

Data collection

Rigaku R-Axis RAPID diffractometer
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.800, T_{max} = 0.889
15118 measured reflections

3546 independent reflections
2751 reflections with I > 2σ(I)
R_{int} = 0.026
θ_{max} = 27.5°
h = −8 → 9
k = −28 → 28
l = −12 → 12

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.041
wR(F²) = 0.117
S = 1.05
3546 reflections
203 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.0644P)² + 0.3702P]
where P = (F_o² + 2F_c²)/3
(Δσ)_{max} = 0.001
Δρ_{max} = 0.32 e Å^{−3}
Δρ_{min} = −0.27 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

V1—O1	1.5846 (17)	O2—N1	1.366 (3)
V1—O2	1.8224 (17)	O3—C5	1.300 (2)
V1—O3	1.9374 (15)	N1—C2	1.290 (3)
V1—O5	1.8386 (15)	N2—N3	1.386 (2)
V1—O5 ⁱ	2.3046 (15)	N2—C3	1.291 (3)
V1—N2	2.1087 (18)	N3—C5	1.316 (2)
V1—O5—V1 ⁱ	106.14 (7)	O2—V1—O5 ⁱ	80.37 (7)
O1—V1—O2	100.45 (10)	O2—V1—N2	80.82 (8)
O1—V1—O3	100.40 (8)	O3—V1—O5 ⁱ	80.38 (6)
O1—V1—O5	102.33 (8)	O3—V1—N2	74.81 (7)
O1—V1—O5 ⁱ	176.15 (7)	O5—V1—O3	90.32 (7)
O1—V1—N2	93.93 (8)	O5—V1—O5 ⁱ	73.86 (7)
O2—V1—O3	148.79 (8)	O5—V1—N2	159.77 (7)
O2—V1—O5	107.53 (8)	N2—V1—O5 ⁱ	89.91 (6)

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

All H atoms were placed in calculated positions and were allowed to ride on their parent C atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq} for aromatic H atoms, and C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq} for methyl H atoms.

Data collection and cell refinement: *RAPID-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); structure refinement and publication material: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976).

The authors thank the National Natural Science Foundation of China (No. 20101003), the Scientific Fund of Remarkable Teachers of Heilongjiang Province (No. 1054 G036) and Heilongjiang University for supporting this study.

References

- Butler, A. & Walker, J. V. (1993). *Chem. Rev.* **93**, 1937–1944.
- Chen, W., Gao, S. & Liu, S.-X. (1999). *Acta Cryst.* **C55**, 531–533.
- Crans, D. C., Keramidas, A. D., Hoover-Litty, H., Anderson, O. P., Miller, S. M., Lemoine, L. M., Pleasic-Williams, S., Vanderberg, M., Rossomando, A. J. & Sweet, L. J. (1997). *J. Am. Chem. Soc.* **119**, 5447–5448.
- Gao, S., Deng, Z.-P., Huo, L.-H. & Zhao, H. (2005). *Acta Cryst.* **E61**, o124–o126.
- Gao, S., Liu, J.-W., Huo, L.-H. & Zhao, H. (2004). *Acta Cryst.* **E60**, m1722–m1724.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Huo, L.-H., Gao, S., Liu, J.-W., Li, J. & Ng, S. W. (2004). *Acta Cryst.* **E60**, m758–m760.
- Huo, L.-H., Gao, S., Liu, J.-W., Zhao, H. & Ng, S. W. (2004). *Acta Cryst.* **E60**, m606–m608.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Martinez, J. S., Carrol, G. L., Tschirret-Guth, R. A., Altenhoff, G., Little, R. D. & Butler, A. (2001). *J. Am. Chem. Soc.* **123**, 3289–3294.
- Rehder, D. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 148–167.
- Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
- Rowe, R. & Jones, M. M. (1957). *Inorg. Synth.* **5**, 113–115.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.