Inorg. Chem. **1998,** *37,* 3119−3121 **3119**

[(μ-OCH$_3$)VO(ma)]$_2$, a Strongly Antiferromagnetic Oxovanadium(IV) Dimer

Yan Sun, Marco Melchior, David A. Summers, Robert C. Thompson,* Steven J. Rettig, and Chris Orvig*

Medicinal Inorganic Chemistry Group, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada

Received December 9, 1997

Introduction

Studies of the detailed oxidation kinetics[1] and solution EPR properties[2] of the potent insulin mimic[3] bis(maltolato)oxovanadium(IV) (VO(ma)$_2$—see Scheme 1) led to the unexpected discovery of a new maltolato dimer, [(μ-OCH$_3$)VO(ma)]$_2$ (ma$^-$ is the maltolato ligand (3-oxy-2-methyl-4*H*-pyran-4-onato-*O*^{3},*O*^{4})).

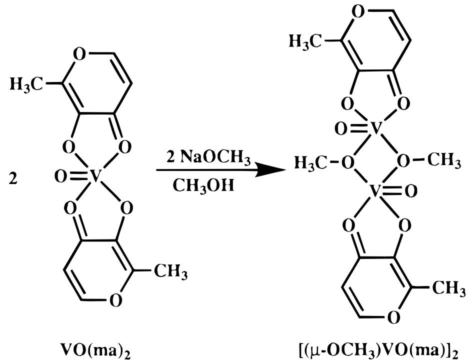
In this note, the synthesis of [(μ-OCH$_3$)VO(ma)]$_2$ by the alcoholysis of VO(ma)$_2$ in methanol is described and the X-ray structure of [(μ-OCH$_3$)VO(ma)]$_2$ is reported. This dimer was found to contain a planar rectangular [(O=V)$_2$O$_2$] core consisting of methoxy-bridged *trans*-oxovanadium(IV) moieties. Two maltolato ligands complete the distorted O$_5$ square pyramid of each oxovanadium(IV) moiety, producing an overall chairlike conformation for the molecule.

Variable-temperature (2−300 K) magnetic susceptibility measurements show strong antiferromagnetism ($J = -107$ cm^{-1}) for this dimer. Mixed-ligand oxovanadium(IV) dimers with solvent-derived bridging ligands are ubiquitous in the coordination chemistry of vanadium; examples include the solid-state structures of hydroxy-,[4] oxo-,[5,6] and alkoxy-bridged[7] species which have been reported.

Experimental Section

Materials and Methods. All manipulations were conducted under an atmosphere of dinitrogen. All chemicals were reagent grade and were used as received. VO(ma)$_2$ was synthesized as described previously.[3] Infrared (IR) spectra were recorded as KBr disks in the range 4000−400 cm^{-1} on a Mattson Galaxy 5000 Series FTIR and were referenced to polystyrene. Analyses for C and H were carried out by Mr. Peter Borda in this department. The room-temperature magnetic moment was measured on a Johnson Matthey MSB-1 balance. Variable-temperature magnetic susceptiblity data were obtained in the range 2−300 K at a field of 10 000 G using a Quantum Design (MPMS) SQUID magnetometer. The sample holder, made from PVC, was specially designed to possess a constant cross-sectional area. Susceptibilities were corrected for sample holder background signal over the entire temperature range studied, and a diamagnetic correction of -95×10^{-6} cm^3 mol^{-1} was applied to the susceptibilities calculated on a per mole of vanadium basis.

Scheme 1



Preparation of [(μ-OCH$_3$)VO(ma)]$_2$. To a mixture of Na (0.076 g, 3.33 mmol) and CH$_3$OH (180 mL) was added solid VO(ma)$_2$ (1.00 g, 3.15 mmol). This mixture was stirred at room temperature for 10 h, yielding [(μ-OCH$_3$)VO(ma)]$_2$, a gray powder, which was isolated by filtration, washed with CH$_3$OH (3 × 20 mL), and dried under vacuum (yield 0.183 g, 26% based on V). Purple-green crystals suitable for an X-ray structural determination were deposited from MeOH/CH$_2$Cl$_2$ (5:1) solutions over a period of 1 month. Anal. Calcd (found) for C$_{14}$H$_{16}$O$_{10}$V$_2$: C, 37.69 (37.65); H, 3.61 (3.61). IR (cm^{-1}; KBr disk): 983 ($\nu_{\mathrm{V=O}}$). μ_{eff}(RT) = 2.07 μ_{B}.

X-ray Crystallographic Analysis of [(μ-OCH$_3$)VO(ma)]$_2$. Selected crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares calculations on the setting angles for 25 reflections with $2\theta = 34.2-45.2°$. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, showed only small random fluctuations. The data were processed[8] and corrected for Lorentz and polarization effects and for absorption (empirical; based on azimuthal scans).

The structure was solved by direct methods. The dinuclear molecule is situated at a crystallographic inversion center. The non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were refined with isotropic thermal parameters. No correction for secondary extinction was necessary. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the refs 9 and 10, respectively. Selected bond lengths and bond angles appear in Table 2. Complete tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, hydrogen atom parameters, anisotropic thermal parameters, bond lengths and angles involving hydrogens, torsion angles, intermolecular contacts, least-squares planes, and C−H···O interactions are included in the Supporting Information.

Results and Discussion

The centrosymmetric dimer [(μ-OCH$_3$)VO(ma)]$_2$ possesses a planar rectangular core of asymmetrically methoxy-bridged *trans*-[VO(ma)]$^+$ units separated by a V−V distance of 3.0806(6) Å (Figure 1). The parallel planes defined by the maltolate ligands are inclined at an angle of 22.25° from the plane defined

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* To whom correspondence should be addressed. R.C.T.: tel, 604-822-4979; fax, 604-822-2847; internet, thompson@chem.ubc.ca. C.O.: tel, 604-822-4449; fax, 604-822-2847; internet, orvig@chem.ubc.ca.

(1) Sun, Y.; James, B. R.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1996**, *35*, 1667.

(2) Hanson, G. R.; Sun, Y.; Orvig, C. *Inorg. Chem.* **1996**, *35*, 6507.

(3) Caravan, P.; Gelmini, L.; Glover, N.; Herring, F. G.; Li, H.; McNeill, J. H.; Rettig, S. J.; Setyawati, I. A.; Shuter, E.; Sun, Y.; Tracey, A. S.; Yuen, V. G.; Orvig, C. *J. Am. Chem. Soc.* **1995**, *117*, 12759.

(4) Dean, N. S.; Bond, M. R.; O'Connor, C. J.; Carrano, C. J. *Inorg. Chem.* **1996**, *35*, 7643.

(5) Duan, A.; Schmidt, M.; Young, V. G., Jr.; Xie, X.; McCarley, R. E.; Verkade, J. G. *J. Am. Chem. Soc.* **1996**, *118*, 5302.

(6) Mohan, M.; Bond, M. R.; Otieno, T.; Carrano, C. J. *Inorg. Chem.* **1995**, *34*, 1233.

(7) Musiani, M. M.; Milani, F.; Graziani, R.; Vidali, M.; Casellato, U.; Vigato, P. A. *Inorg. Chim. Acta* **1982**, *61*, 115.

(8) *teXsan*: *Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1992.

(9) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99−102.

(10) *International Tables for Crystallography*; Kluwer Academic Publishers, Boston, MA, 1992; Vol. C, pp 200−206.

S0020-1669(97)01549-8 CCC: $15.00

Table 1. Crystallographic Data for $[(\mu\text{-OCH}_3)\text{VO(ma)}]_2$

formula	$C_{14}H_{16}O_{10}V_2$	Z	2
fw	446.16	ρ_{calc}, g/cm^3	1.668
crystal system	monoclinic	T, °C	21
space group	$P2_1/n$	radiation	Mo
a, Å	8.9260(7)	λ, Å	0.710 69
b, Å	11.014(1)	μ, cm^{-1}	10.66
c, Å	9.362(1)	transm factors (rel)	0.84−1.00
β, deg	105.239(7)	R^a	0.035
V, Å^3	888.0(1)	$R_w{}^b$	0.033

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(\mu\text{-OCH}_3)\text{VO(ma)}]_2$

V(1)−O(2)	1.938(1)	V(1)−O(3)	2.017(1)
V(1)−O(4)	1.967(1)	V(1)−O(4)*	1.946(1)
V(1)−O(5)	1.588(1)	V(1)−V(1)*	3.0806(6)
O(2)−V(1)−O(3)	81.46(5)	O(2)−V(1)−O(4)	89.25(6)
O(2)−V(1)−O(4)*	137.93(6)	O(2)−V(1)−O(5)	111.68(7)
O(3)−V(1)−O(4)	148.04(6)	O(3)−V(1)−O(4)*	90.47(5)
O(3)−V(1)−O(5)	104.21(7)	O(4)−V(1)−O(4)*	76.15(5)
O(4)−V(1)−O(5)	107.64(7)	O(4)*−V(1)−O(5)	110.33(7)

* Symmetry operation $-x$, $-y$, $-z$.

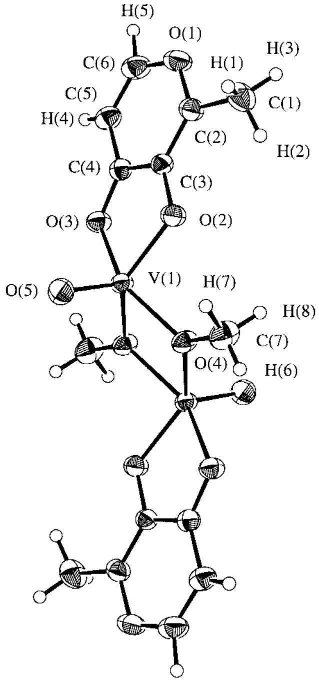

Figure 1. ORTEP representation (33% probability ellipsoids) for non-hydrogen atoms and labeling scheme of $[(\mu\text{-OCH}_3)\text{VO(ma)}]_2$.

by the rectangular core, producing an overall chairlike conformation for the molecule. Each vanadium atom possesses a distorted square pyramidal geometry, defined by the O_5 coordination set, with the vanadium atom 0.610 Å from the basal plane defined by O(2), O(3), O(4), and O(4)*. The $[\text{VO(ma)}]^+$ unit of the dimer, consisting of the oxovanadium (IV) moiety and the maltolato ligand, is essentially identical to the $[\text{VO(ma)}]^+$ unit in the parent compound VO(ma)_2.[3] The oxo−vanadium bond lengths (1.596(7) Å for VO(ma)_2 compared to 1.588(1) Å for V(1)−O(5)) and the ligand bite angles (81.46° for VO(ma)_2 compared with 81.5° for O(3)−V(1)−O(1)), as well as the V−O distances (2.024(8) and 1.958(8) Å for the ketonic and enolic V−O distances, respectively, of VO(ma)_2 compared to 2.017(1) and 1.938(1) Å for V(1)−O(3) and V(1)−O(2) of the dimer), are not significantly different. The structure of the $[\text{VO(ma)}]^+$ unit is conserved even with a radical change in coordination environment, implying that the structure of the $[\text{VO(ma)}]^+$ species, which has been shown to predominate at low pH (~2−3) by solution potentiometric[3] and EPR studies,[2] probably possesses this isostructural $[\text{VO(ma)}]^+$ motif. Similar compounds of other ligands have been reported, including $[(\mu\text{-OCH}_3)\text{VO(acac)}]_2$[7], which differs in the key respect that it possesses a symmetrically bridged square $[(\text{O=V})_2\text{O}_2]$ core but possesses a similar chairlike orientation.

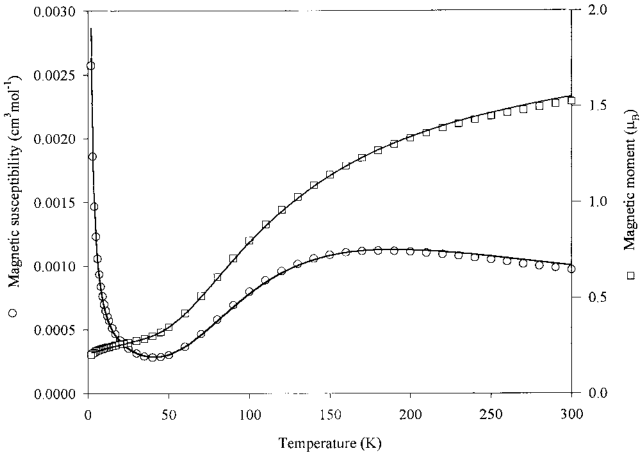

Figure 2. Plots of magnetic susceptibility and magnetic moment on a per mole of vanadium basis vs temperature. Lines are best-fit to theory as described in the text.

Magnetic susceptibilities plotted versus temperature (Figure 2) clearly show a broad maximum around 150−200 K, consistent with the presence of significant antiferromagnetic coupling. The increase in susceptibilities with decreasing temperature in the very low temperature region is often seen in strongly antiferromagnetically coupled systems[11] and arises from a small amount of paramagnetic impurity in the sample. The magnetic susceptibilities were fitted to eq 1 for antiferromagnetically coupled $S = {}^1/_2$ dimers[12] with allowance for a paramagnetic fraction P and temperature-independent paramagnetism (TIP).

$$\chi = \frac{2Ng^2\beta^2}{kT}\left[(1-P)\left[\frac{\exp(2J/kT)}{1+3\exp(2J/kT)}\right]+\frac{P}{4}\right]+\text{TIP} \qquad (1)$$

In modeling the data, g was set at 2.00 and J, P, and TIP were allowed to vary. The best fit values of $-J$, P, and TIP were 107 cm^{-1}, 0.015, and 0.000 135 cm^3 mol^{-1}, respectively. The best fit was the one which minimized the function F in eq 2. The value of F, which provided a measure

$$F = \left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\chi_{calc}{}^{i} - \chi_{obs}{}^{i}}{\chi_{obs}{}^{i}}\right)^2\right]^{1/2} \qquad (2)$$

of agreement between experimental data and the model, was 0.027 in this case.

It is interesting to compare the magnitude of J obtained for this maltolato complex ($-J = 107$ cm^{-1}) with values reported earlier for related citrato[11] and 3-hydroxy-2-glutarato[13] complexes. Using the convention of ligands on the x and y axes, and z coincident with V=O, the magnetic orbitals on each of the metal ions in these complexes are the d_{xy} orbitals, and this

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(11) Burojevic, S.; Shroeky, I.; Bino, A.; Summers, D. A.; Thompson, R. C. *Inorg. Chim. Acta* **1996**, *251*, 75.

(12) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, 226.

(13) Castro, S. L.; Cass, M. E.; Hollander, F. J.; Bartley, S. L. *Inorg. Chem.* **1995**, *34*, 466.

configuration favors direct metal−metal exchange over ligand-mediated superexchange.[14]

In such geometries as the *trans*-$[(O{=}V)_2O_2]$ conformation found in $[(\mu\text{-OCH}_3)VO(ma)]_2$, the magnitude of this exchange is expected to be related directly to the V−V distance; this is indeed observed.[15,19] As the V−V distance decreases from 3.107 Å in the glutarato complex[13] to 3.0806 Å in the maltolato complex to 2.949 Å in the citrato complex,[11] the value of $-J$ increases from 30 to 107 to 212 cm^{-1}.[15]

Conclusion

The alcoholysis of the potent insulin mimic $VO(ma)_2$ yields $[(\mu\text{-OCH}_3)VO(ma)]_2$, which crystallizes as a centrosymmetric dimer possessing a planar rectangular $[(O{=}V)_2O_2]$ core consisting of methoxy-bridged *trans*-oxovanadium(IV) moieties. The individual $[VO(ma)]^+$ units are structurally identical to those found in the parent compound $VO(ma)_2$, and temperature-dependent magnetic susceptibility measurements are indicative of a strongly antiferromagnetically coupled ($-J = 107$ cm^{-1}) oxovanadium(IV).

Acknowledgment is made to the Medical Research Council of Canada for an operating grant (C.O.) and to the Natural Sciences and Engineering Research Council for fellowships (Y.S., M.M.) and an operating grant (R.C.T.). We also thank Professor J. Trotter for the very kind use of his crystallographic facilities and one reviewer for particularly insightful comments.

Supporting Information Available: Detailed tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, hydrogen atom parameters, anisotropic thermal parameters, bond lengths and angles involving hydrogens, torsion angles, intermolecular contacts, least-squares planes, and C−H···O interactions (13 pages). Ordering information is given on any current masthead page.

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(14) Hasty, E. F.; Colburn, T. J.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 2414.

(15) One reviewer pointed out that this simple magnetostructural correlation between V−V distance and the value of $-J$ can be expanded to include three additional dinuclear oxovanadium(IV) compounds, all of which are single atom di-μ-oxo-bridged $(VO)_2(O)_2$ units with anti-oriented oxo groups, as in the title compound. These compounds are $[(VO)_2(tacn)_2(\mu\text{-OH})_2]^{2+}$,[16] $\{K_2[(VO)_2(L)]\}_n$,[17] and $[VO(HB(pz)_3)(\mu\text{-OH})]_2$.[18]

(16) Wieghardt, K.; Bossek, U.; Volckmar, K.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 1387.

(17) Solari, E.; Klose, A.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Polyhedron* **1996**, *15*, 4103.

(18) Dean, N. S.; Bond, M. R.; O'Connor, C. J.; Carrano, C. J. *Inorg. Chem.* **1996**, *35*, 7643.

(19) Plass, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 627.