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The Oxo−Vanadium(IV) Dimer of 3-Hydroxy-3-methylglutarate: X-ray Crystal Structure, Solid State Magnetism, and Solution Spectroscopy

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Reaction of vanadyl sulfate with 3-hydroxy-3-methylglutarate yields a complex which was shown by X-ray crystallography to be a vanadium−oxo dimer. The structure has two 3-hydroxy-3-methylglutarate trianions acting as tridentate ligands, each bridging the vanadiums through the hydroxy oxygen and each bonding to the different vanadiums through carboxylate oxygens. A temperature dependent magnetism study on the crystalline complex shows that the two vanadium(IV) $S = {}^1/_2$ centers are antiferromagnetically coupled with a coupling constant of $J = -30$ cm^{-1}, μ_{expt} (298K) = 0.6 μ_B/vanadium. The V=O stretching frequency in the IR was assigned for the complex using oxygen exchange in ^{18}O labelled water: (V=^{16}O appears at 976 cm^{-1}). Crystal data: $Na_2[VO(OOCCH_2CO(CH_3)CH_2COO)]_2 \cdot 3H_2O \cdot CH_3OH$, $V_2Na_2O_{16}C_{13}H_{24}$, orthorhombic, space group = $Pn2_1a$, a = 18.032(3) Å, b = 10.071(3) Å, c = 12.899(3) Å, V = 2342.3(16) Å^3, Z = 4, 1630 observed unique data, R = 5.07%, R_w = 6.04%, all measurements at −130 °C.

Introduction

In this paper we report the solid state temperature dependent magnetism, solution spectroscopy and X-ray crystal structure of the disodium salt of $[(VO)(3\text{-hydroxy-3-methylglutarate})]_2{}^{2-}$. Synthesis of complexes with vanadium coordinated to deprotonated carboxylate and hydroxyl functional groups has been actively investigated by several research groups as a means of gaining insight into biologically relevant vanadium chemistry.[1] Our study of the vanadium coordination chemistry of the 3-hydroxy-3-methylglutarate ligand (Figure 1a) stems from our interest in synthetic analogues of the naturally occurring vanadium(IV) compound isolated from the mushroom *Amanita muscaria*, an organism known to sequester vanadium from its environment. In *Amanita muscaria*, vanadium is chelated using the *N*-hydroxy-2,2′-iminodipropionic acid ligand (Figure 1b, R = CH_3). Two equivalents of this ligand bind to vanadium to form a very stable complex.[2] Two possible coordination geometries for the 2:1 complex were originally proposed: The oxo−vanadium(IV) complex shown in Figure 1c and the unusual octacoordinate V(IV) complex shown in Figure 1d in which each of the two ligands binds in a tetradentate fashion through two carboxylate oxygens and both the N and O of the *N*-hydroxy functional group.[2,3] In 1988, Frausto da Silva *et al.* published a crystal structure of the V(IV) complex of *N*-hydroxy-2,2′-iminodiacetic acid (Figure 1b, R = H).[4] This ligand indeed binds to vanadium(IV) giving the unusual octacoordinate complex proposed for the natural product. Since the vanadium(IV) complexes of *N*-hydroxy-2,2′-iminodipropionic acid and *N*-hydroxy-2,2′-diacetic acid show very similar EPR and IR spectra, both were believed to be octacoordinate complexes.[2,5] In 1991, the octacoordinate geometry for the V(IV) complex of the *N*-hydroxy-2,2′-iminodipropionic acid ligand was confirmed by an X-ray crystallographic structure determination carried out by Garner *et al.*[6] More recently, Garner *et al.* published the X-ray crystal structure for the essentially isostructural V(V) complex of this ligand.[7]

The 3-hydroxy-3-methylglutaric acid ligand used in this study can bind to vanadium through two carboxylate oxygens; however it lacks the nitrogen atom found in the naturally occurring sequestering agent. Not unexpectedly, the absence of nitrogen in the ligand results in a significantly different observed coordination chemistry. Our research shows that 3-hydroxy-3-methylglutaric acid favors the formation of a dimeric structure. This ligand uses the deprotonated hydroxy oxygen of the alcohol functional group to bridge two adjacent vanadium(IV) centers (Figure 1e). Furthermore, the two

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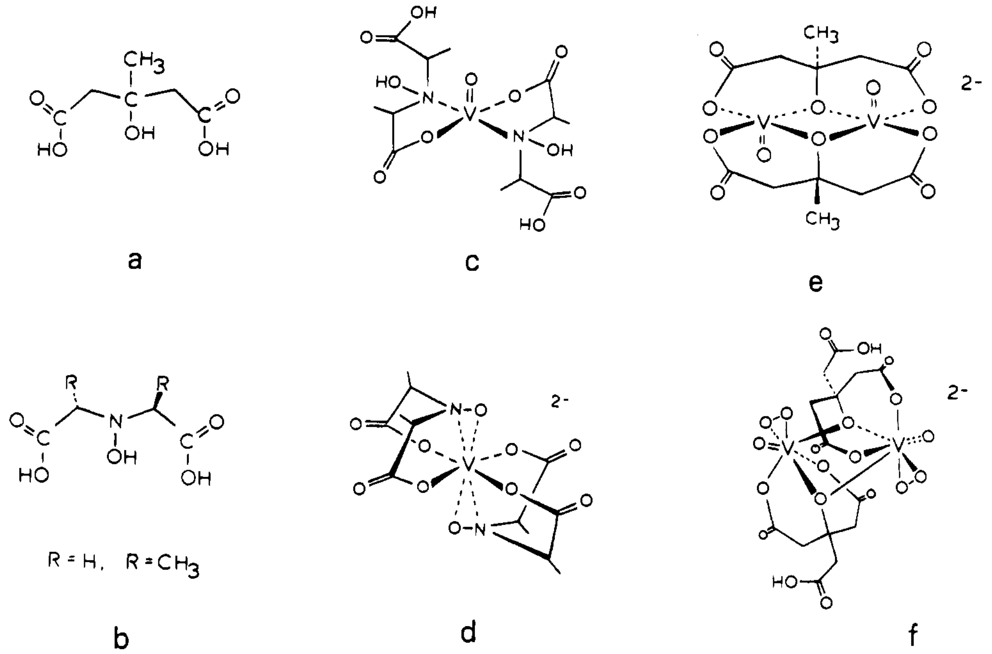

Figure 1. Structures of ligands and complexes discussed in this study.

V(IV) $S = {}^1/_2$ metal centers antiferromagnetically couple through this bridging deprotonated hydroxy oxygen. Use of the deprotonated oxygen atoms of hydroxy or phenoxy groups to bridge two vanadium ions has been reported in the dimeric complexes of a number of different multidentate ligands.[8] An example of one such structure, the [(oxo)(peroxo)(citrato)vanadium(IV)] dimer, is illustrated in Figure 1f.[9]

In addition to coordination through the bridging hydroxy group, each metal in the dimer of the 3-hydroxy-3-methylglutarate ligand is bound to two different ligands through one oxygen of one carboxylate group. Carboxylate groups have been observed to coordinate to vanadium(IV) through one or both oxygen atoms, although in most reported structures of complexes with multifunctional ligands, carboxylate groups bind through a single oxygen.[8] In the dimeric complex of the 3-hydroxy-3-methylglutaric acid ligand, a fifth coordination site on the metal is occupied by an oxo ligand. The sixth coordination site, trans to the oxo ligand, is vacant. Each metal center is pentacoordinate with a very commonly found square pyramidal coordination geometry.

Experimental Section

Materials and Methods. All chemicals were obtained from Aldrich Chemical Co. unless otherwise noted and were used without further purification. Labeled ^{18}Oxygen water was obtained from Merck Sharp and Dohme. Syntheses were carried out under argon using Schlenk line and inert atmosphere techniques.

Synthesis of $Na_2[VO(OOCCH_2CO(CH_3)CH_2COO)]_2$. Vanadyl sulfate ($VOSO_4 \cdot 3H_2O$, 0.0872 g, 0.402 mmol) and 3-hydroxy-3-methylglutaric acid (0.1311 g, 0.8086 mmol) were combined in 2 mL of distilled H_2O to yield a light blue solution. Upon addition of 1.65 mL of 1 M KOH, the solution turned a deep purple-blue color. The reaction mixture was stirred for 3 h and then lyophilized to yield a purple-blue solid. This solid was used in subsequent solution IR studies. Alternatively, $Na_2[VO(OOCCH_2CO(CH_3)CH_2COO)]_2$ was synthesized in methanol. Vanadyl sulfate ($VOSO_4 \cdot 3H_2O$, 0.0436 g, 0.201 mmol), 3-hydroxy-3-methylglutaric acid (0.0653 g, 0.403 mmol), and Na_2CO_3 (0.0863 g, 0.814 mmol) were added to 2 mL of methanol. The solution was stirred for several hours (4–8), and a purple-blue precipitate was obtained upon filtration. The precipitate was dissolved in the minimum amount of water and brought to a pH of 6 with 1 M HCl. Crystals were grown by slow vapor diffusion of methanol into the saturated aqueous solution of the product. This crystalline product was used in subsequent X-ray crystallography, EPR, and magnetism experiments. Elemental analyses for three samples of crystalline solid were carried out by Galbraith Laboratories: Anal. Found (calcd) for $V_2Na_2O_{16}C_{13}H_{24}$: V, 16.47, 15.94, 17.22 (17.4%); C, 23.61, 26.31, 23.77, (26.73); H, 3.97, 3.40, 3.57 (4.1); Na, 9.68, 7.55, 8.46, (7.87).

Temperature Dependent Magnetism Studies. The magnetic susceptibility of 29.80 mg of a ground sample of crystalline $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2 \cdot 3H_2O \cdot CH_3OH$ was measured as a function of temperature from 2 to 400 K using a Quantum Designs Squid susceptometer device at Michigan State University. The temperature dependent study was carried out at a field strength of 1000 G. A correction for the sample container was measured prior to beginning the experiment (diamagnetic correction for the sample container: -2.89×10^{-5} emu).

Solution Infrared Studies. IR spectra were recorded in aqueous solution on a Mattson Instruments 4020 Galaxy Series FT-IR. Aqueous solutions were placed in a cylindrical internal reflection cell ("Circle" Liquid Analyzer, Spectra Tech, Inc.). Background spectra of distilled water or ^{18}O water were subtracted from the spectra as appropriate, using Mattson FIRST software.

Solution EPR Studies. EPR spectra of aqueous solutions contained in a quartz flat cell were recorded at room temperature on a Bruker 203ER EPR spectrometer (University of Minnesota, Minneapolis). Calibrated spectrometer frequency was 9.747 GHz. Spectra were referenced to an external standard of DPPH (diphenylpicrylhydrazide). Spectra were recorded on both powdered solid samples and crystalline samples dissolved in aqueous solution. (Solution concentrations: 0.0189 mg of $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2 \cdot 3H_2O \cdot CH_3OH$ was dissolved in 0.30 mL of deionized distilled water 5 min before recording the EPR spectrum). Instrument conditions were set for those of previously run samples of $[V(N,N\text{-hydroxyiminodiacetate})_2]^{2-}$ which gave strong signals under those conditions. Six solutions of $[V(N,N\text{-hydroxyiminodiacetate})_2]^{2-}$ were prepared between 0.0077 and 0.193 M. Signal to noise ratios in the EPR varied accordingly (a 0.0077 M solution gave a signal to noise ratio of 11:1, and a 0.193 M solution gave a signal to noise ratio of 70:1).

X-ray Crystallography. Data Collection. Purple-blue bladelike crystals of the compound were obtained by slow crystallization from

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[8] (a) Rehder, D., *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 148–167. (b) Boas, L. V.; Pessoa, J. C. In *Comprehensive Coordination Chemistry*, Wilkinson, G., ed.; Pergamon Press: New York, 1987; Vol. 3, pp 454–583.

[9] Djordjevic, C.; Lee, M.; Sinn, E. *Inorg. Chem.* **1989**, *28*, 719.

Table 1. Crystal and Data Parameters for $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2{\cdot}CH_3OH{\cdot}3H_2O$[a,b]

empirical formula: $V_2Na_2O_{16}C_{13}H_{24}$	fw = 584.2
$a = 18.032(3)$ Å	space group: $Pn2_1a$
$b = 10.071(3)$ Å	$T = -130$ °C
$c = 12.899(3)$ Å	$\lambda(\text{Mo K}\alpha) = 0.71073$ Å
$V = 2342.3(16)$ Å^3	$d(\text{calc}) = 1.66$ g/cm^3
$Z = 4$	$\mu(\text{calc}) = 8.8$ cm^{-1}
	$R = 5.07\%$
	$R_w = 6.04\%$

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Kα components of 24 reflections with 2θ between 28 and 30°. [b] In this and all subsequent tables the esd's of all parameters are given in parentheses, right justified to the least significant digit(s) of the reported value.

methanol/water. Fragments cleaved from some of these crystals were mounted on glass fibers using Paratone N hydrocarbon oil.

The crystal used for data collection was transferred to the Enraf-Nonius CAD-4 diffractometer at the University of California, Berkeley,[10] and centered in the beam. The crystal was cooled to −130 °C (±5°) by a nitrogen flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the sample position. Automatic peak search and indexing procedures yielded an orthorhombic reduced primitive cell. Inspection of the Niggli values[11] revealed no conventional cell of higher symmetry. The final cell parameters and specific data collection parameters for this data set are given in Table 1.

Structure Determination. The 1782 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background and Lorentz and polarization effects.[12-14] Inspection of the intensity standards revealed a slow increase of 7% of the original intensity. The data were corrected for this "decay". Inspection of the azimuthal scan data[15] showed a variation *Imin/Imax* = 0.94 for the average curve. An empirical correction based on the observed variation was applied to the data. Inspection of the systematic absences indicated possible space groups *Pnma* and $Pn2_1a$. The choice of the acentric group (albeit in a nonstandard setting) was confirmed by the successful solution and refinement of the structure. Removal of systematically absent data left 1630 unique data in the final data set.

The structure was solved by direct methods using the SHELXS program and refined via standard least-squares and Fourier techniques. The structure solution and refinement was hampered by disorder of various types (see below). The final difference fourier map showed no reliable indications of hydrogen atom positions, so they were not included in structure factor calculations. One reflection (50−2) was removed from the data set due to an apparent measuring error.

The final residuals[16] for 293 variables refined against the 1359 data for which $F^2 > 3\sigma(F^2)$ were $R = 5.07\%$, $R_w = 6.04\%$, and GOF = 2.07. The R value for all 1629 accepted data was 6.44%. In the final cycles of refinement a secondary extinction parameter[17] was included (maximum correction −8% on F).

The quantity minimized by the least squares program was $\Sigma(w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p-factor,[16] used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used[18] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[19] The largest peak in the final difference Fourier map had an electron density of 0.56 e/Å^3, and the lowest excursion −0.26 e/Å^3.

The positional and anisotropic thermal parameters of the atoms are available as supplementary material.

Results and Discussion

Addition of an excess of 3-hydroxy-3-methylglutaric acid to a vanadyl starting material produces a 2:2 vanadyl:glutarate dimeric complex. The complex is highly water soluble and maintains its purple-blue color in aqueous solution. The dianionic complex crystallizes as a sodium salt. The X-ray structure determination shows that each vanadium(IV) ion in the dimer is pentacoordinate with a square pyramidal coordination environment. Each vanadium is bonded to one oxo ligand, to two deprotonated carboxylate oxygens of different glutarate ligands, and to the two deprotonated 3-hydroxy groups of the ligands which sit in bridging positions between the two vanadium metal centers. An ORTEP drawing of one molecule is shown in Figure 2.[20] Final values of the refined atomic coordinates are presented in Table 2. Intramolecular bond distances and angles are given in Table 3 and 4 respectively.

Four isomeric forms of the dimeric complex co-crystallized within the single crystal examined by X-ray diffraction. The four isomers are divided into two subsets defined as either *cis* or *trans* with respect to the orientation of the two oxo ligands.

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(10) Instrumentation at the University of California Chemistry Department X-ray Crystallographic Facility (CHEXRAY) consists of two Enraf-Nonius CAD-4 diffractometers, one controlled by a DEC PDP 8/a with an RK05 disk and the other by a DEC PDP 8/e with a RL01 disk. Both use Enraf-Nonius software as described in *CAD4 Operation Manual*; Enraf-Nonius: Delft, The Netherlands, Nov 1977, updated Jan 1980.

(11) Roof, R. B., Jr. *A Theoretical Extension of the Reduced-Cell Concept in Crystallography*; Publication LA-4038, Los Alamos Scientific Laboratory: Los Alamos, NM, 1969.

(12) Calculations were performed on DEC Microvax II using locally modified Nonius-SDP3 software operating under the Micro-VMS operating system.

(13) *Structure Determination Package User's Guide*, B. A. Frenz and Associates, Inc.: College Station, TX, 1985.

(14) The data reduction formulas are as follows:

$$F_o^{\,2} = \frac{\omega}{L_p}(C - 2B) \qquad \sigma_o(F_o^{\,2}) = \frac{\omega}{L_p}\sqrt{C + 4B}$$

$$F_o = \sqrt{F_o^{\,2}} \qquad \sigma_o(F) = \sqrt{F_o^{\,2} + \sigma_o(F_o^{\,2})} - F_o$$

where C is the total count in the scan, B the sum of the two background counts, ω is the scan speed used in deg/min and

$$\frac{1}{L_p} = \frac{\sin 2\theta\,(1 + \cos^2 2\theta_m)}{1 + \cos^2 2\theta_m - \sin^2 2\theta}$$

is the correction for Lorentz and polarization effects for a reflection with scattering angle 2θ and radiation monochromatized with a 50% perfect single-crystal monochrometer with scattering angle $2\theta_m$.

(15) Reflections used for azimuthal scans were located near x = 90° and the intensities were measured at 10° increments of rotation of the crystal about the diffraction vector.

(16) Here

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|} \qquad R_w = \sqrt{\frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^{\,2}}}$$

$$GOF = \sqrt{\frac{\sum w(|F_o| - |F_c|)^2}{(n_o - n_v)}}$$

where n_o is the number of observations, n_v the number of variable parameters, and the weights w were given by

$$w = \frac{1}{\sigma^2(F_o)} \qquad \sigma(F_o^{\,2}) = \sqrt{\theta_o^{\,2}(F_o^{\,2}) + (pF^2)^2}$$

where $\sigma^2(F_o)$ is calculated as above from $\sigma(F_o^2)$ and where p is the factor used to lower the weight of intense reflections.

(17) Zachariesen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139.

(18) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography;* The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(19) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography;* The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(20) Johnson, C. K., *Report ORNL-3794*; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

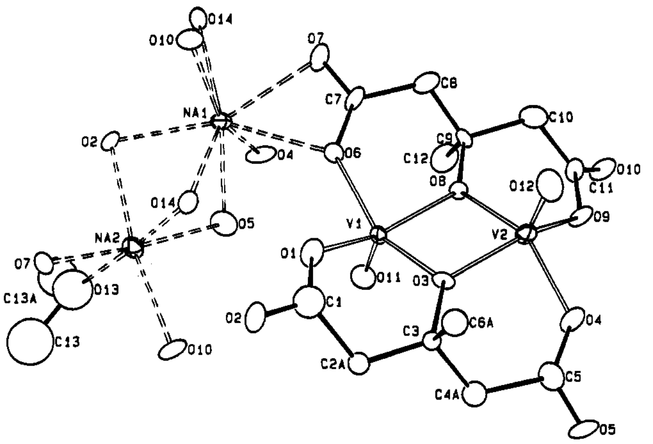

Figure 2. ORTEP plot showing the anti-parallel-*trans* dimer and the two unique sodium ions and their environment. The disordered "water" molecules are not shown. Glutarate ligand 1 is shown in its "antiparallel" configuration. Atomic elipsoids are scaled to represent a 50% probability surface.

Table 2. Atomic Coordinates for $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2 \cdot CH_3OH \cdot 3H_2O$

atom	*x*	*y*	*z*	occupancy
V1	0.6881(1)	0.3580(1)	0.1821(1)	0.91
V1A	0.639(1)	0.370(2)	0.276(1)	0.09
V2	0.77230(9)	0.3322(2)	0.3913(1)	
Na1	0.5394(2)	0.5962(4)	0.0079(3)	
Na2	0.5226(2)	0.3448(5)	−0.1516(3)	
O1	0.5981(4)	0.2508(8)	0.1637(6)	
O2	0.5325(4)	0.0642(7)	0.1518(6)	
O3	0.7182(4)	0.2282(7)	0.2883(5)	
O4	0.8360(4)	0.1768(7)	0.4135(7)	
O5	0.8728(4)	−0.0288(8)	0.3944(6)	
O6	0.6241(4)	0.5144(7)	0.1584(6)	
O7	0.5889(4)	0.7213(7)	0.1586(6)	
O8	0.7419(4)	0.4622(7)	0.2861(5)	
O9	0.8627(3)	0.4430(7)	0.4075(6)	
O10	0.9260(4)	0.6260(7)	0.3944(6)	
O11	0.7394(4)	0.342(1)	0.0832(5)	0.91
O11A	0.589(5)	0.37(1)	0.346(7)	0.09
O12	0.7223(4)	0.3530(9)	0.4907(5)	
O13	0.5345(5)	0.330(1)	−0.3290(8)	
O14	0.4963(3)	0.3474(8)	0.0244(5)	
C1	0.5872(7)	0.127(1)	0.182(1)	
C2	0.620(1)	0.071(3)	0.290(2)	0.50
C2A	0.666(1)	0.050(2)	0.185(2)	0.50
C3	0.7035(5)	0.086(1)	0.2860(8)	
C4	0.735(1)	0.026(2)	0.390(2)	0.50
C4A	0.780(1)	0.026(2)	0.282(2)	0.50
C5	0.8255(7)	0.057(1)	0.383(1)	
C6	0.736(1)	0.029(3)	0.185(2)	0.50
C6A	O.660(1)	0.054(2)	0.382(2)	0.50
C7	0.6281(6)	0.636(1)	0.193(1)	
C8	0.6740(6)	0.664(1)	0.293(1)	
C9	0.7502(6)	0.602(1)	0.2861(8)	
C10	0.7925(6)	0.642(1)	0.387(1)	
C11	0.8665(6)	0.570(1)	0.3942(9)	
C12	0.7944(7)	0.642(1)	0.190(1)	
C13	0.518(2)	0.216(4)	−0.393(3)	0.60
C13A	0.547(2)	0.405(5)	−0.407(3)	0.40
O101	0.426(4)	0.165(7)	0.328(6)	0.20
O102	0.385(2)	0.259(3)	0.418(3)	0.35
O103	0.410(2)	0.013(3)	0.460(2)	0.35
O104	0.487(2)	0.543(4)	0.392(3)	0.35
O105	0.481(2)	0.423(5)	0.331(3)	0.30
O106	0.427(2)	0.297(3)	0.325(3)	0.35

Table 3. Intramolecular Distances Å in $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2 \cdot CH_3OH \cdot 3H_2O$

V1−O1	1.963(9)	Na1−O2	2.455(9)
V1−O3	1.970(8)	Na1−O4	2.681(10)
V1−O6	1.976(8)	Na1−O5	2.497(10)
V1−O8	1.960(8)	Na1−O6	2.604(9)
V1−O11	1.584(8)	Na1−O7	2.482(9)
V1A−O1	2.022(25)	Na1−O10	2.421(9)
V1A−O3	2.024(24)	Na1−O14	2.632(10)
V1A−O6	2.120(24)	Na1−O14	2.644(10)
V1A−O8	2.076(23)		
V1A−O11A	1.28(10)	Na2−O2	2.423(9)
		Na2−O5	2.351(9)
V2−O3	1.953(8)	Na2−O7	2.366(9)
V2−O4	1.962(8)	Na2−O10	2.463(10)
V2−O8	1.964(8)	Na2−O13	2.303(12)
V2−O9	1.987(8)	Na2−O14	2.320(7)
V2−O12	1.581(8)		
V1−V2	3.107(3)		
V1A−V2	2.85(2)		

Table 4. Intramolecular Angles (deg) in $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2 \cdot CH_3OH \cdot 3H_2O$

O1−V1−O3	86.9(3)	V1−O1−C1	129.7(9)
O1−V1−O6	86.4(4)	V1A−O1−C1	120.3(11)
O1−V1−O8	141.8(4)	V1−O3−V2	104.8(4)
O1−V1−O11	109.3(5)	V1−O3−C3	126.1(7)
O3−V1−O6	142.9(4)	V1A−O3−V2	91.5(7)
O3−V1−O8	75.1(3)	V1A−O3−C3	124.3(10)
O3−V1−O11	109.4(4)	V2−O3−C3	129.2(7)
O6−V1−O8	88.1(3)	V2−O4−C5	128.1(9)
O6−V1−O11	107.2(5)	V1−O6−C7	131.6(8)
O8−V1−O11	108.4(4)	V1A−O6−C7	113.3(10)
O1−V1A−O3	83.9(10)	V1−O8−V2	104.7(4)
O1−V1A−O6	81.2(8)	V1A−O8−V2	89.6(7)
O1−V1A−O8	129.5(11)	V1−O8−C9	125.8(7)
O1−V1A−O11A	104.6(53)	V1A−O8−C9	122.6(10)
O3−V1A−O6	129.0(11)	V2−O8−C9	129.3(7)
O3−V1A−O8	71.5(7)	V2−O9−C11	125.8(9)
O3−V1A−O11A	116.8(55)		
O6−V1A−O8	81.5(9)		
O6−V1A−O11A	114.1(55)		
O8−V1A−O11A	125.7(53)		
O3−V2−O4	88.0(4)		
O3−V2−O8	75.4(3)		
O3−V2−O9	141.5(4)		
O3−V2−O12	109.8(4)		
O4−V2−O8	142.8(4)		
O4−V2−O9	87.3(3)		
O4−V2−O12	108.7(5)		
O8−V2−O9	85.8(3)		
O8−V2−O12	108.2(4)		
O9−V2−O12	108.0(4)		

Each of the two *cis* isomers and each of the two *trans* isomers are then differentiated from one another by the orientation of one of the bound glutarate ligands (ligand 1; carbon atoms C1−C6). The two orientations of ligand 1 are referred to as being "parallel" or "antiparallel" depending on the relative position of the methyl group on ligand 1, defined by the C3−C6 vector, to the position of the methyl group on ligand 2, defined by the C9−C12 vector. The second glutarate ligand (ligand 2; carbon atoms C7−C12) has only one orientation in the crystal. The four isomers of the dimer in the crystal are thus "parallel-*cis*" (present at approximately 5% occupancy, Figure 3a), "parallel-*trans*" (present at approximately 45%, Figure 3c), "antiparallel-*cis*" (present at approximately 5%, Figure 3b) and "antiparallel-*trans*" (present at approximately 45%, Figure 3d).

The presence of the four isomers gives rise to two observed disorders in the crystal. The first disorder, resulting from the *cis* and *trans* forms, was modelled by refining one vanadyl group in two positions: V1 and O11 were refined with occupancy factors of 0.91 for the *trans* forms, and V1A and O11A with occupancy factors of 0.09 for the *cis* forms. The second vanadyl group, V2 and O12, showed no disorder. The second observed disorder appears to be a 50:50 mixture of two orientations of ligand 1. Carbons 2, 4, and 6 of ligand 1 (C2, C2A, C4, C4A, C6, and C6A) were refined with occupancy factors of 0.50 to model this disorder. The structure with ligand 1 assigned as

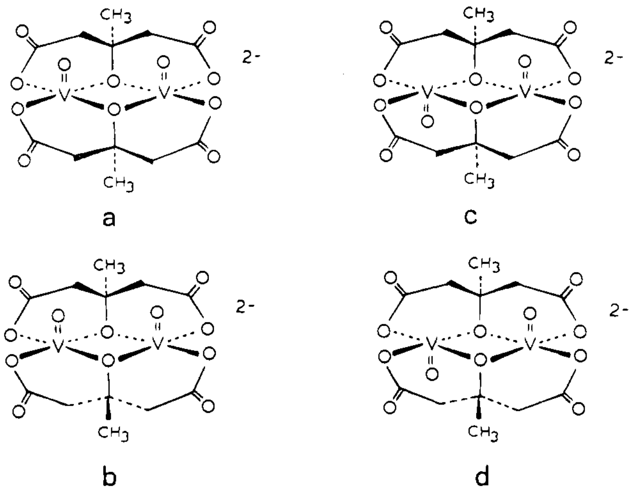

Figure 3. Structures of the four isomeric vanadyl dimers.

C1, C2, C3, C4, C5, and C6 has the dimer in the parallel-*cis* and parallel-*trans* configurations. The structure with ligand 1 assigned as C1, C2A, C3, C4A, C5, and C6A has the dimer in the antiparallel-*cis* and antiparallel-*trans* configurations.

The overall structure of the crystal consists of dianions of composition $[(VO)(3\text{-hydroxy-3-methylglutarate})]_2^{2-}$ linked together into a three-dimensional structure by chains of sodium ions which are additionally coordinated and bridged by oxygen atoms from the glutarate ligands, a water molecule, and a methanol molecule. Two positions of the CH_3 group (C13, C13A) of the methanol molecule were modeled in a 60:40 ratio. In addition there are water molecules contained loosely within a cavity generated by the three dimensional structure. These disordered water molecules were modeled by refining six partially occupied oxygen positions (O101−O106) representing a total of two additional water molecules per complex. The overall composition of the crystal is $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2 \cdot 3H_2O \cdot CH_3OH$.

Infrared vibration frequencies for the V=O stretch of known V(IV) oxo species have been reported at 950−1000 cm^{-1}.[21] Solid state and solution spectra of our complexes are complicated by ligand vibrations in this frequency region. The exchange of the vanadium bound ^{16}O oxo ligand for ^{18}O allowed us to definitively assign the V=O stretching frequency region for the glutarate complex(es).[22] In our experiment solid sodium bis[(3-hydroxy-3-methylglutarate)oxovanadate(IV)] was dissolved in 97% $^{18}OH_2$ and reflectance IR spectra were recorded every thirty minutes for three hours. A spectrum taken immediately after dissolution in $^{18}OH_2$ (dashed line) and a spectrum recorded 3 h later (solid line) are contrasted in Figure 4. Comparison of the spectra shows the disappearance of a broad resonance with a maximum at 976 cm^{-1} accompanied by the appearance of a broad peak with a maximum at 935 cm^{-1}. The theoretical shift in frequency predicted by Hooke's law of the V=O stretch upon exchange of ^{16}O in the oxo ligand for ^{18}O is 42 cm^{-1}. The experimentally observed shift of 41 cm^{-1} is well within the uncertainty limits of the spectrometer (± 2 cm^{-1}). A broad band of frequencies in the V=O region is consistent with the presence of several vanadium oxo species in solution. The X-ray crystallography has established that four isomeric forms of the complex are formed. Group theory analysis suggests that up to seven V=O stretches could be observed arising from the four dimeric forms of the complex: two from the *trans*-parallel configuration, (Figure 3c, C_1 symmetry), one V=O stretch from the *trans*-antiparallel configuration (Figure 3d, C_i symmetry), and two V=O stretches from each of the configurations with *cis* oxo ligands (the *cis*-parallel configuration (Figure 3a) and the *cis*-antiparallel configuration (Figure 3b), both having C_s symmetry).

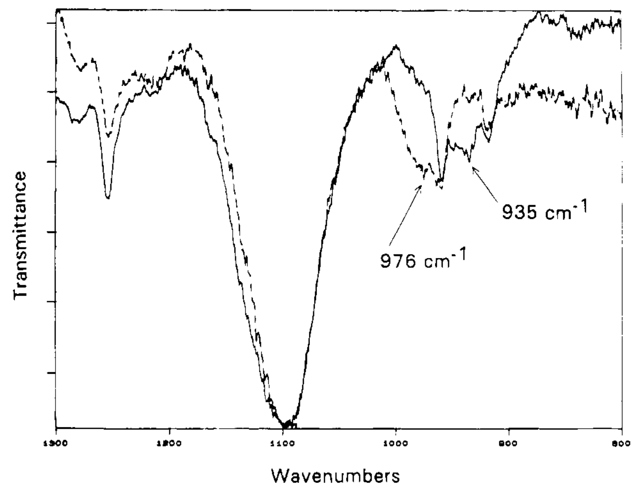

Figure 4. Oxo ligand exchange experiment: infrared spectra of $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2$ dissolved in $^{18}OH_2$, (- -) 10 min after the crystalline solid was dissolved in ^{18}O labeled water and (—) 3 h later. The spectrum of pure $^{18}OH_2$ was subtracted from each spectrum.

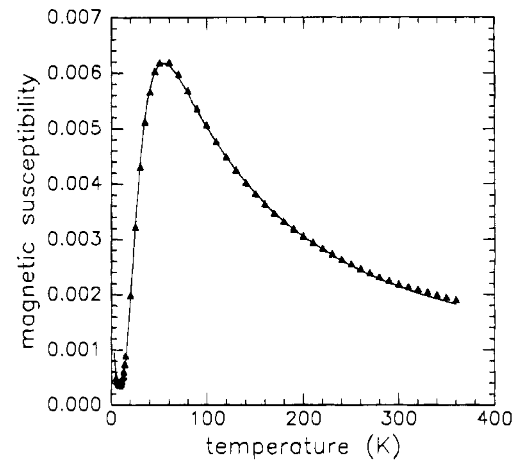

Figure 5. Magnetic susceptiblity as a function of temperature: (▲) experimental data; (—) calculated fit with $J_{\text{trans}} = -30(1)$ cm^{-1}. See reference 25.

Measurement of the magnetic susceptibility of a ground sample of crystalline $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2 \cdot 3H_2O \cdot CH_3OH$ as a function of temperature clearly exhibited behavior characteristic of an antiferromagnetically coupled system with a maximum magnetic susceptibility observed at 55 K. A plot of magnetic susceptibility verses temperature is shown in Figure 5. The magnetic susceptibility was corrected for diamagnetic effects ($\chi_{\text{diamagnetic}} = -2.33 \times 10^{-4}$ emu)[23] and fit to the Hamiltonian for the interaction between two $S = {}^1/_2$ spins on adjacent atoms i and j (where the coupling constant J is positive for a ferromagnetically coupled system and negative

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(21) Cotton, F. A.; Wilkinson, G., *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1988; p 672.

(22) The exchange rate of ^{18}O for ^{16}O of the oxo ligand in $VO^{2+}(aq)$ has been measured; $t_{1/2} = 400$ min at 0 °C. (a) Johnson, M. D.; Murmann, R. K. *Inorg. Chem.* **1983**, *22*, 1068. (b) Gamsjager, H.; Murmann, R. K. *Advances in Inorganic and Bioinorganic Mechanisms;* Sykes, A. G., Ed.; Academic Press: New York, 1983, Vol. 2, pp 317−380.

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Table 5. Magnetic Properties of Reported Vandium Dimers

complex	V–V dist, Å	magnetic properties	ref
1. Antiferromagnetically Coupled Dimers			
trans-$[(V^{IV}O)_2$(*N*-(2-hydroxyphenyl)-3-bromosalicylidenamine]	not reported	$2J = -115$ cm^{-1}	31
bis(hydridotripyrazoylborato)(*μ*-hydroxo)bis(*μ*-carboxylato)$(V^{III})_2$	3.410	$J = -31.3$ cm^{-1}	30
cis-$[(V^{IV}O)_2(\mu\text{-}OH)_2$-*N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine]	2.965	$J = -150$ cm^{-1}	32
trans-$[(V^{IV}O)_2(\mu\text{-}OH)_2$(1,4,7-triazacyclononane)$_2]Br_2$	3.033	$J = -177$ cm^{-1}	33
cis-$[(V^{IV}O)_2$(2-(salicylideneamino)-1-hydroxyethane)$_2$]	3.068	$\mu_{expt} = 1.52\ \mu_B/V$	34
trans-$Na_2[(V^{IV}O)$(3-hydroxy-3-methylglutarate)]$_2$	3.107	$J = -30$ cm^{-1} $\mu_{expt} = 0.6\ \mu_B/V$	this work
2. Weakly Coupled Vanadium Centers in Dimers			
[HB(3,5-(Me)$_2$pyrazoyl)$_3$]$(V^{IV}O)$-(*μ*-malonate)$(V^{IV}O)$-(3,5-(Me)$_2$pyrazoyl)[HB(3,5-(Me)$_2$pyrazoyl)$_3$]	not reported	$J \approx -3$ cm^{-1}	35
3. Magnetically Noninteracting V Centers in Dimers			
[*cis*-$(V^{IV}O)_2$-*μ*-(*N,N',N'',N'''*-(2-acetyl-1-buten-3-one)tetraaminobenzene)]	8.66	$J = 0$ cm^{-1}	36
4. Ferromagnetically Coupled Vanadium Dimers			
bis(hydridotripyrazoylborato)(*μ*-oxo)bis(*μ*-carboxylato)$(V^{III})_2$	3.264	$\mu_{expt} = 3.47\ \mu_B/V$	30

for an antiferromagnetically coupled system).

$$\hat{H} = -2J\hat{S}_i\cdot\hat{S}_j$$

This expression was solved for one set of *trans*-$(VO)_2$ complexes (present at approximately 91%, as indicated by the crystal structure determination), and one set of *cis*-$(VO)_2$ complexes (present at approximately 9% as indicated by the crystal structure determination) each set with two $S = {}^1/_2$ centers antiferromagnetically coupling as a function of temperature with respective coupling constants of J_{trans} and J_{cis}.[24] A term was added for an $S = {}^1/_2$ paramagnetic impurity present at 0.75% which gives rise to an increase in the magnetic susceptibility below 10 K.

$$\chi_m = \chi_{observed} - \chi_{diamagnetic}$$

$$\chi_m = \left[\frac{Ng^2\beta^2}{kT}\right]\left[(0.91)\frac{2e^{2J_{trans}/kT}}{1 + 3e^{2J_{trans}/kT}} + (0.09)\frac{2e^{2J_{cis}/kT}}{1 + 3e^{2J_{cis}/kT}}\right] + (0.0075)\left[\frac{Ng^2\beta^2}{4kT}\right]$$

The trans coupling constant (J_{trans}) was roughly calculated from the Neel temperature giving a value close to -30 cm^{-1} (-6.0×10^{-15} erg). Experimental data was fit to this expression varying J_{trans}, J_{cis}, and g using the fitting program GENPLOT.[25] We report the value of $J_{trans} = 6.0(\pm 2) \times 10^{-15}$ erg ($=-30(\pm 1)$ cm^{-1}), the average value from two calculated fits: one where g was allowed to vary and a second where g was not allowed to vary.[26] We are not comfortable reporting a value for J_{cis} since it is present in such low concentration. The magnetic moment at 298 K was calculated from the measured magnetic susceptibility to be $\mu_{expt} = 1.19\ \mu_B$ for the dimer and $\mu_{expt} = 0.6\ \mu_B$/vanadium.

Dimeric vanadium(IV) oxo species exhibit four different types of magnetic behavior: (1) Antiferromagnetically coupled complexes arise from strong electron spin interactions.[27] (2) Noninteracting magnetically equivalent oxo–vanadium(IV) moieties in the same molecule result when no electron spin–electron spin interactions occur. These dimers give rise to EPR spectra that are indistinguishable from those of simple $S = {}^1/_2$ monomers.[27] (3) Intermediate cases are also observed with weak electron spin–electron spin interactions.[27–29] (4) Ferromagnetically coupled vanadium dimers can also arise from strong electron spin interactions. A ferromagnetically coupled vanadium(III) dimer has been recently reported.[30] Examples of several vanadium dimers and their magnetic properties are shown in Table 5.[30–36] The temperature dependent magnetic susceptibility experiment on $Na_2[(VO)$(3-hydroxy-3-methylglutarate)]$_2CH_3OH{\cdot}3H_2O$ has allowed us to establish that this dimer falls into the category of a more strongly antiferromagnetically coupled dimer ($J_{trans} = -30$ cm^{-1}).

The observed antiferromagnetism in $Na_2[(VO)$(3-hydroxy-3-methylglutarate)]$_2$ is consistent with its structure. The two vanadyl moieties are in close proximity (the V1–V2 distance is 3.107(3) Å in the *trans* isomers and the V1A–V2 distance is 2.85(2) Å in the *cis* isomers). Furthermore, the coplanar arrangement of the basal ligand planes of the two square pyramidal vanadium(IV) ions forces the d_{xy} orbitals into an orientation that is nearly coplanar. Despite the fact that the vanadium ions are displaced from the basal O_4 ligand planes (in the trans isomers the vanadiums are displaced 0.6 Å in opposite directions, and in the cis isomers, both vanadium ions are displaced in the same direction; 0.6 Å for V2 and 0.86 Å for V1A), the two basal O_4 ligand planes of the two metal ions in each dimer are less than 1° from coplanar. This type of geometry allows the d_{xy} orbitals on adjacent metal ions to be alligned with the correct symmetry to participate in direct overlap and hence magnetic exchange.[27,36]

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(24) Drago, R. S., *Physical Methods for Chemists*, 2nd ed.; Saunders College Publishing: New York, 1992; pp 469–494.

(25) *GENPLOT*, A Data Analysis and Graphics Program for Scientists and Engineers. Copyright 1988–1991, Computer Graphic Service, Ltd., Ithaca, NY.

(26) The value of J_{trans} was determined to be $-5.88(\pm 2) \times 10^{-15}$ erg when J_{trans}, J_{cis}, and g were allowed to vary [giving the best fit shown in Figure 5 with $J_{trans} = -5.88(\pm 2) \times 10^{-15}$ erg $= -29.7$ cm^{-1}, $g = 1.93(\pm 1)$ and $J_{cis} = -1.4(\pm 2) \times 10^{-14}$ erg $= -73$ cm^{-1}. The parameter CHISQR was minimized in the fit, CHISQR $= 2.4 \times 10^{-9}$]; J_{trans} was found to be $-6.10(\pm 2) \times 10^{-15}$ erg when J_{trans} and J_{cis} were allowed to vary and g was held constant at 2.0023 (CHISQR $= 6.0 \times 10^{-9}$), and $J_{trans} = -6.05(\pm 2) \times 10^{-14}$ when J_{trans} was constrained to be equal to J_{cis} and both were allowed to vary along with g [$g = 1.89$ (an unacceptably low value), CHISQR $= 6.2 \times 10^{-9}$].

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No electron paramagnetic resonance (EPR) signal was detected when a 0.11 M aqueous solution of a crystalline sample of $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2\cdot 3H_2O\cdot CH_3OH$ was examined under conditions which gave strong signals for a monomeric $[V(N\text{-hydroxy-}N,N\text{-iminodiacetate})_2]^{2-}$ complex. A 0.0077 M solution of $[V(N\text{-hydroxy-}N,N\text{-iminodiacetate})_2]^{2-}$ (greater than an order of magnitude more dilute) gave a clear eight line pattern indicative of ^{51}V hyperfine coupling and a signal to noise ratio of 11:1 under identical experimental conditions. At very high gain, the room temperature spectrum of a 0.20 M solution of unrecrystallized $Na_2[(VO)(3\text{-hydroxy-3-methylglutarate})]_2$ shows a very weak eight line pattern indicative of electron coupling to an $I = {}^7/_2$ ^{51}V species superimposed upon a broad background. The calculated values of $g_o = 1.968$ and $A_o = 1.872 \times 10^{-18}$ erg $= 9.42 \times 10^{-3}$ cm^{-1} ($a_o = 102.6$ G) are consistent with those observed for monomeric square-pyramidal oxo−vanadium(IV) complexes, in which all five coordination sites on the vanadium are occupied by oxygen atoms.[37] We believe that this very low intensity signal results from a paramagnetic impurity in the unrecrystallized product. Evidence of a very low concentration paramagnetic impurity is also observed at low temperatures (2−10 K) in the magnetic susceptibility experiment.

Conclusions

The reaction of vanadyl ion with 3-hydroxy-3-methylglutaric acid yields a product which crystallizes as the sodium salt of a dimeric oxovanadium(IV) dianion; $[(VO)(3\text{-hydroxy-3-methylglutarate})_2]^{2-}$. The X-ray structure determination shows that each 3-hydroxy-3-methylglutarate ligand is fully deprotonated and acts as a tridentate ligand. The two deprotonated carboxylate oxygens on each glutarate ligand bind to different vanadiums ions and the deprotonated hydroxy oxygen on each ligand bridges the two vanadium centers. Infrared spectroscopy indicates that oxo−vanadium(IV) species exist when the dimer is dissolved in aqueous solution. A broad band with a maximum at 976 cm^{-1} was assigned to the V=O stretching frequencies by exchange of the ^{16}O oxo ligand(s) for ^{18}O in $^{18}OH_2$. Electron paramagnetic resonance spectroscopy suggests that essentially no EPR active species are present in a recrystallized sample dissolved in aqueous solution at room temperature and a small but detectable level of a monomeric oxo−vanadium(IV) species is present at room temperature in aqueous solutions of the unrecrystallized material. Temperature dependent magnetic susceptibility measurements clearly demonstrate that the dimeric forms of the complex contain two V(IV) $S = {}^1/_2$ metal centers, antiferromagnetically coupled with a coupling constant of $J_{\text{trans}} = -30(\pm 1)$ cm^{-1} and an experimentally determined magnetic moment of $\mu_{\text{expt}} = 0.6\ \mu_B$/vanadium.

Acknowledgment. We thank the Research Corp. (Grant No. C-2509) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 20705-GB3), for support of this research. M.E.C. thanks Larry Que of the University of Minnesota and Frank Rusnak of the Mayo Clinic for helpful discussions on magnetic properties and student colleagues Kyle Garton and Kevin Cook for their help with the concentration studies on related vanadium(IV) monomers.

Supplementary Material Available: Tables of final positional parameters with esd's, bond lengths, bond angles, rms amplititudes of anisotropic displacements, anisotropic thermal parameters, and least squares planes and dihedral angles (4 pages). Ordering information is given on any current masthead page. A table of observed and calculated structure factors is available upon request from the authors.

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