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A Tetranuclear Vanadium(III, III, IV, IV) Complex Formed by a Reaction of Bis(acetylacetonato)oxovanadium(IV) with a Thiolate Ligand

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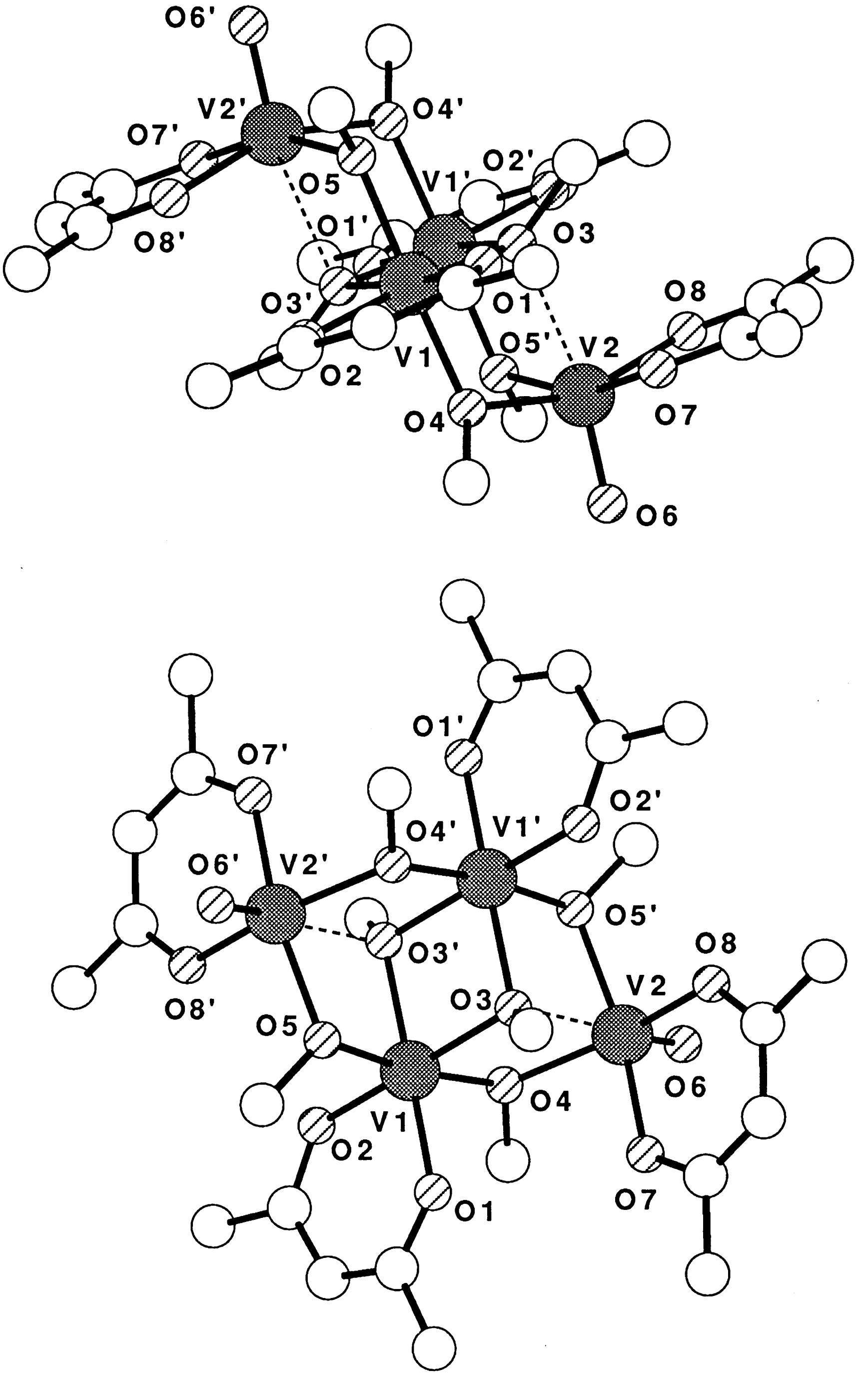
A mixed-valence tetranuclear vanadium(III, III, IV, IV) complex, $[V_2(VO)_2(acac)_4(CH_3O)_6]$ (Hacac=acetylacetone), has been isolated by a reaction of $VO(acac)_2$ with 2-(3-aminopropylamino)ethanethiol in methanol-dichloromethane. The complex has been characterized by X-ray structure analysis, XPS and electronic spectra, and magnetic susceptibilities (80—300 K).

The chemistry of vanadium complexes has been the subject of extensive study over the past decade since their biological1,2) and industrial3) significance has been recognized. Recent biological results for nitrogenase from several species of nitrogen-fixing bacteria suggest that the vanadium-sulfur interaction is important for the nitrogenase activity.2) Therefore vanadium thiolate complexes are also of current interest as the possible model compounds. Thiolate groups take part in many biological redox reactions, including reduction of a metal ion by a thiol. In the course of our investigations on metal-thiolate complexes, we have described some properties and crystal structures of thiolate-bridged nickel and manganese complexes.4-9) In an effort to extend our system to vanadium chemistry, we have found that a novel tetranuclear vanadium complex is formed by a reaction of bis(acetylacetonato)oxovanadium(IV) with a thiolate ligand. Although this complex does not contain any thiolate ligands, this is a novel mixed-valence complex and the structural feature is the first example for tetranuclear vanadium complexes. We herein report the isolation, X-ray crystal structure, XPS (X-ray photoelectron spectroscopy) spectra, electronic spectra, and magnetic properties of the tetranuclear vanadium complex, $[V_2(VO)_2(acac)_4(CH_3O)_6]$ (**1**).

The tetranuclear complex **1** was isolated as follows, with all operations being performed under an Ar atmosphere using standard Schlenk line techniques. After dissolving bis(acetylacetonato)oxovanadium(IV) (99 mg, 0.37 mmol) and 2-(3-aminopropylamino)ethanethiol (50 mg, 0.37 mmol) in a methanol-dichloromethane (1:1) solution, the mixture was heated for 30 min and then filtered. The filtrate was allowed to stand for several days at room temperature. Dark brown plates were deposited and collected by filtration.10) A similar reaction employing other thiolate ligand such as 2-aminoethanethiol leads to the same tetranuclear complex.

The molecular structure of **1** was determined by X-ray crystallography.11) Perspective views of the molecular structure of **1** are shown in Fig. 1. The complex contains a crystallographic inversion center at the midpoint between the V1 and V1' atoms or the V2 and V2' atoms. The four V atoms occupy the corners of a diamond shape: V1-V1' 3.109(2) Å, V1-V2 3.273(2) Å, V1-V2' 3.279(2) Å, and V2-V2' 5.768(2) Å. The V1 and V1' atoms are bridged by two methoxo-oxygen atoms (O3 and O3') forming a dinuclear plane with acetylacetonato ligands. This methoxo-bridged dinuclear unit is further bound to the two acetylacetonatooxo-



V2-O3	2.359(5)Å	V1-O1	1.997(6)Å	V1-V1'	3.109(2)Å
V2-O4	2.018(5)	V1-O2	1.996(5)	V1-V2	3.273(2)
V2-O5'	2.018(6)	V1-O3	2.045(5)	V1-V2'	3.279(2)
V2-O6	1.596(5)	V1-O3'	2.042(5)	V2-V2'	5.768(2)
V2-O7	1.994(6)	V1-O4	1.970(5)	V1-O3-V1'	99.0(2)°
V2-O8	1.985(5)	V1-O5	1.979(5)	V1-O4-V2	110.4(2)
				V1-O5-V2'	110.4(2)

Fig. 1. Perspective views of $[V_2(VO)_2(acac)_4(CH_3O)_6]$ (**1**).

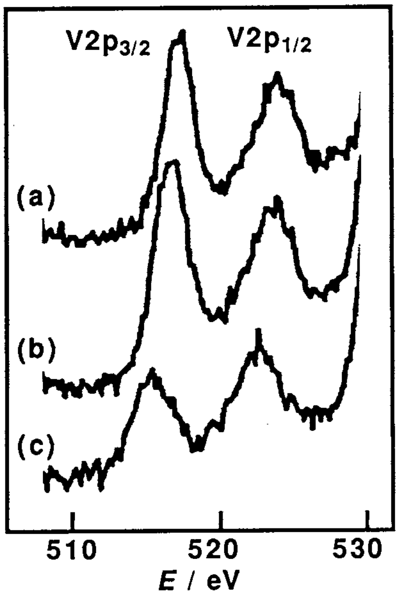


Fig. 2. The XPS spectra of (a) $VO(acac)_2$, (b) $[V_2(VO)_2(acac)_4(CH_3O)_6]$ (**1**), and (c) $V(acac)_3$.

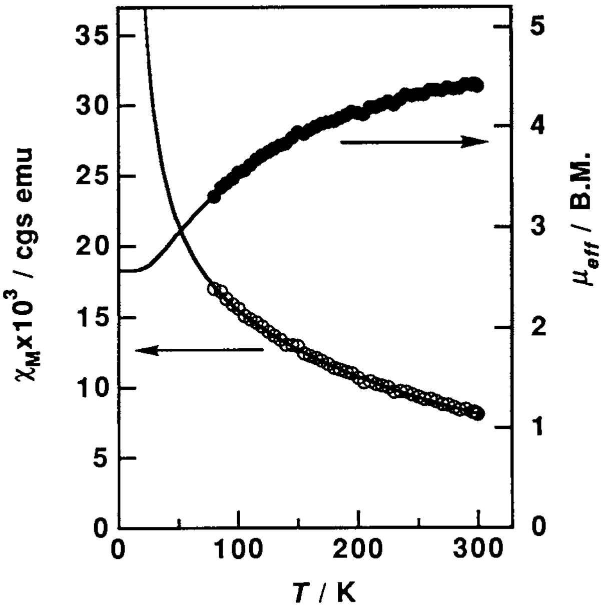


Fig. 3. Temperature dependence of the magnetic moments and magnetic susceptibilities of **1**.

vanadium moieties through the methoxo-bridges above and below the dinuclear plane. The coordination geometry around V1 is a compressed octahedron. The V1-O distances are in the range 1.970(5)—2.045(5) Å, and are comparable to those of $V(acac)_3$ (V-O 1.979, 1.982 Å).[12] The V2 atom is in a square-pyramidal environment. The in-plane V2-O distances range from 1.985(5) to 2.018(5) Å; they agree well with those reported for vanadium(III) complexes with β-diketonato ligands (V-O 1.95—1.99 Å).[12] The apical V2-O6 bond is 1.596(5) Å and indicates considerable double bond character. This is similar to those found for bis(β-diketonato)oxovanadium(IV) complexes (1.56—1.62 Å).[12] The double bond character may be confirmed by the infrared spectrum of **1**. An intense band at 975 cm^{-1} was assigned to the stretching vibration due to ν(V=O). The methoxo-oxygen O3 can be considered to be involved in the μ_3-bridge among the V1, V1', and V2 atoms. The V2-O3 bond distance trans to the V=O bond is significantly longer than the other V-O bonds. This is due to the trans-influence of the V=O group and has been observed in many oxovanadium complexes.[12] The consideration of overall anion charge necessitates the mixed-valence description vanadium(III, III, IV, IV). Although the V-O bond distances for the V1 and V2 atoms are similar, a simple calculation of the bond-valence parameters obtained from the crystal structure database[13] permits differentiation between the two oxidation states; the V1 and V1' atoms are V^{III}, while the V2 and V2' atoms are V^{IV}. This is further supported by the fact that an oxovanadium form has never been found for vanadium(III) ion, but for vanadium(IV) state.[12]

In order to examine the mixed-valence state, the XPS spectrum of **1** was measured along with the spectra of $VO(acac)_2$ and $V(acac)_3$.[14] The V2p3/2 and V2p1/2 binding energies of **1** are 515.6 and 522.7 eV, respectively, being significantly higher than those of the V(III) species, $V(acac)_3$ (V2p3/2 at 514.6 eV and V2p1/2 at 522.1 eV). Although the binding energies are slightly lower than those of $VO(acac)_2$ (V2p3/2 at 515.8 eV and V2p1/2 at 523.0 eV), the spectral features are close to those of the V(IV) species, $VO(acac)_2$ (Fig. 2). The XPS results seem to be hard to detect the mixed-spin state.

Diffuse reflectance spectrum of **1** shows weak absorption bands at 307, 470sh, 550sh, and 850 nm. In chloroform, the complex shows a similar spectrum (316 (ε=19600), 414 (ε=1120), 530sh (ε=130), and 876 nm (ε=50 $dm^3mol^{-1}cm^{-1}$ per tetranuclear molecule)). Two lower-energy bands may be assigned to the d-d transitions for the V^{III} and V^{IV} ions.

Temperature dependence of the magnetic susceptibility of **1** was measured over the temperature range 80—300 K. The magnetic moment at room temperature (4.41 B.M./mol) is smaller than the spin-only value (4.69 B.M.) expected for non-interacting d^1-d^2-d^2-d^1 system. The data of the magnetic susceptibility were analyzed by the Van-Vleck equation based on the Heisenberg model, $\mathcal{H} = -2JS_{V1}\cdot S_{V1'}-2J'(S_{V1}\cdot S_{V2}+S_{V1}\cdot S_{V2'}+S_{V1'}\cdot S_{V2}+S_{V1'}\cdot S_{V2'})$ ($S_{V1} = S_{V1'} = 1, S_{V2} = S_{V2'} = 1/2$), and the best fit was obtained by $J = -41.3\ cm^{-1}$, $J' = 0.0\ cm^{-1}$ and $g = 2.10$ (Fig. 3). Thus, a significant antiferromagnetic coupling exists between the V1 and V1' atoms.

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10) A satisfactory analysis (C, H, N) was obtained.
11) Crystal data for **1**: $V_4O_{16}C_{26}H_{46}$, F.W.=818.40, monoclinic, space group $P2_1/n$, a=11.464(5), b=11.995(3), c=13.759(6) Å, β=109.28(2)°, V=1785.9(13) $Å^3$, Z=2, D_m=1.50, D_c=1.52 g cm^{-3}, μ(Mo-Kα=10.45 cm^{-1}, R=0.049, R_w=0.054. For the determination of structure, intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. 3131 reflections were measured in the range $1\le 2\theta \le 46$°; 1600 with $I\ge 3\sigma(I)$ were assumed as observed. The structure was solved by direct methods and refined by the full-matrix least-squares method using the SDP program package.
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14) XPS spectra were measured on a VG Scientific ESCALAB MARKII spectrometer with Mg Kα radiation. The spectra were standardized by the C1s signal of contaminate carbon line for which a binding energy of 284.6 eV was assigned.

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