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Dinuclear Oxovanadium(IV) Thiolate Complexes with Ferromagnetically Coupled Interaction between Vanadium Centers

Yi-Fang Tsai,[†] Gui-Shih Huang,[†] Chen-I Yang,[†] Hui-Lien Tsai,[†] Yi-Hung Liu,[‡] Ting-Shen Kuo,[§] and Hua-Fen Hsu*,[†]

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 701, Department of Chemistry, National Taiwan University, Taipei 116, Taiwan, and Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan

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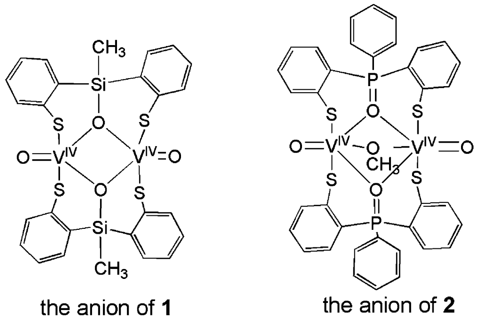
Two dinuclear oxovanadium(IV) thiolate complexes, $[N(C_5H_{11})_4]_2[VOL1]_2$ (**1**) and $[N(C_4H_9)_4][(VOL2)_2(\mu\text{-}OCH_3)]$ (**2**) (where L1 = $[(CH_3)SiO(C_6H_4\text{-}2\text{-}S)_2]^{3-}$ and L2 = $[(C_6H_5)PO(C_6H_4\text{-}2\text{-}S)_2]^{2-}$), have been synthesized and characterized. The geometry of the anion in **1** can be classified to an edge-sharing bi-square-pyramid with a syn-orthogonal configuration. The one in **2** can be view as a face-sharing bioctahedron with two oxo groups in syn positions. Of note, these two complexes display intramolecular ferromagnetic interaction between two metal centers.

Our interest in studying vanadium chemistry stems from its important roles in biological systems as well as its medical application.[1] In particular, VO^{2+} is probably considered as the most relevant species present in biological systems.[2] The interaction of high-valent vanadium species with sulfur-containing bioligands such as cysteine and glutathione is associated with the mechanisms of the following: the protein tyrosine phosphatase inhibition by vanadate,[3] the antidiabetic behavior of vanadium compounds,[4] the redox conversion of vanadium in ascidians,[5] the function of amavadin isolated from *Amanita* mushrooms,[6] and the toxicity of vanadium in biological systems.[7] Against this background, it is very important to understand the fundamental chemical and physical properties of high-valent vanadium complexes in a sulfur-rich ligation environment.[8] Thus, we have been prompted to explore the chemistry of high-valent vanadium species reacting with S-donor ligands. Such efforts have resulted in the isolation of two dinuclear oxovanadium(IV) thiolate complexes, $[N(C_5H_{11})_4]_2[VOL1]_2$ (**1**) and $[N(C_4H_9)_4][(VOL2)_2(\mu\text{-}OCH_3)]$ (**2**) (where L1 = $[(CH_3)SiO(C_6H_4\text{-}2\text{-}S)_2]^{3-}$ and L2 = $[(C_6H_5)PO(C_6H_4\text{-}2\text{-}S)_2]^{2-}$) (Scheme 1). Notably, reported dinuclear oxovanadium(IV) complexes with S-donor ligands are relatively rare compared to those with N,O-donor ligands.[9]

Scheme 1



Interestingly, **1** and **2** both embrace ferromagnetic-interacting divandyl cores, in contrast to most existing examples of dinuclear oxovanadium(IV) compounds, which exhibit antiferromagnetic interaction between two vanadium centers.[10] To elucidate magnetically coupled active sites in metalloproteins and develop magnetic materials, it is essential to have fundamental knowledge pertaining to the magnetic properties of molecular compounds. Even though attention has been paid to the magnetic studies of divanadium(IV)

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* To whom a correspondence should be addressed. E-mail: konopka@mail.ncku.edu.tw.

[†] National Cheng Kung University.

[‡] National Taiwan University.

[§] National Taiwan Normal University.

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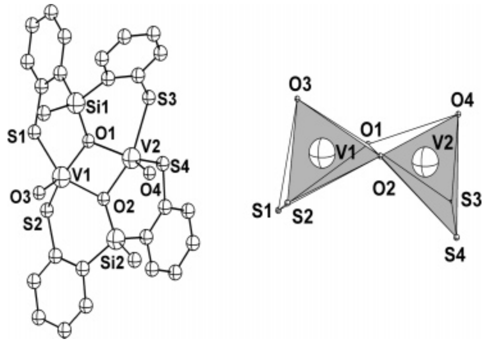

Figure 1. ORTEP diagram and polyhedral diagram of **1** shown with 35% thermal ellipsoids. H atoms and anions are omitted for clarity. Selected bond distances (Å) and angles (deg): V1−O1 2.004(2), V2−O1 1.985(2), V1−O2 1.980(2), V2−O2 2.015(2), V1−O3 1.598(2), V2−O4 1.597(2), V1−S1 2.376(1), V1−S2 2.387(1), V2−S3 2.388(1), V2−S4 2.364(1), V2−V1 3.122(1); S1−V1−S2 79.59(3), S1−V1−O1 92.76(6), S2−V1−O2 90.44(7), O1−V1−O2 76.17(8), S3−V2−S4 80.58(3), S3−V2−O1 89.99(7), S4−V2−O2 91.79(6), O1−V2−O2 75.81(8).

complexes (d^1-d^1),[11] the magnetostructural correlations of this system still remain to be fully explored.

The reaction of $VO(acac)_2$ with $H_3[^{Me}SiS3]$ ($H_3[^{Me}SiS3]$ = $(CH_3)Si(C_6H_4\text{-}2\text{-}SH)_3$) and 3 equiv of $NaOCH_3$ in methanol generated a green solution. The addition of the cation, $[N(C_5H_{11})_4]Br$, to the reaction mixture yielded a green crystalline solid of **1**. The finding of the L1 ligand, bis(benzenethiolato)methylsilanoxide, contained in **1** indicates that the reaction involved a Si−C(phenyl) bond cleavage of $H_3[^{Me}SiS3]$, leading to the formation of silanoxide. The detailed mechanism of this Si−C bond activation is obscure but interesting to unravel. The X-ray crystallographic data show that the anion of **1** consists of two V^{IV}═O units bridged by two silaneoxide groups of L1 ligands (Figure 1).[12] Each V ion also binds to two thiolate groups from two L1 ligands, forming a distorted square-pyramidal geometry ($\tau = 0.25$).[13] Two V ions are displaced from the basal O2−S2 ligand planes: 0.66 Å for V1 and 0.68 Å for V2. The geometry of the anion in **1** could be viewed as an edge-sharing bi-square-pyramid with a dihedral angle of 111.0° between two basal planes (Figure 1). According to the orientation of the V═O groups with respect to the $V_2(\mu\text{-}OR)_2$ plane (OR = silanoxide), the $[VO(\mu\text{-}OR)_2VO]^{2+}$ moiety in **1** can be classified as a syn-orthogonal configuration.[11a] The average V═O and V−S distances are 1.60 and 2.38 Å, respectively, similar to those found in reported V^{IV}═O and vanadium(IV) thiolate complexes.[9,14]

Compound **2** was obtained from the reaction of $VO(i\text{-}PrO)_3$ with $Na_2[^{Ph}PS2]$ (where $^{Ph}PS2 = [(C_6H_5)P(C_6H_4\text{-}2\text{-}S)_2]^{2-}$) in methanol followed by the addition of the cation, $[N(C_4H_9)_4]$-Br. Bis(benzenethiolato)phenylphosphine ($^{Ph}PS2$) was oxidized to bis(benzenethiolato)phenylphosphine oxide (L2) contained in **2**, while V^V was reduced to V^{IV}. The pathway might involve the transformation of an O atom from the vanadium(V) oxo species to $^{Ph}PS2$; however, this needs to be investigated further. The structure of **2**, characterized by X-ray crystallography, consists of two V^{IV}═O units bridged by one methoxide and two phosphine oxide groups of L2 ligands (Figure 2).[15] Bond valence sum (BVS) calculations give values of 3.82, 3.90, and 2.05 for V1, V2, and O4, respectively, confirming the assignment of the oxidation state of the two V^{IV} centers and the bridging methoxide group instead of methanol.[16] Each V ion also binds to two thiolates as terminal ligands, completing a distorted octahedral coordination environment. The two terminal O atoms are both trans to bridging phosphine oxides and syn to each other. Two V ions are displaced toward the terminal O groups: 0.46 Å for V1 and 0.37 Å for V2. The geometry of the anion in **2** can be viewed as two octahedra that share a triangle face composed of three bridging O atoms (O3, O4, and O5) (Figure 2). Such a geometry is not very common for existing dinuclear oxoxvanadium(IV) complexes.[17] The mean equatorial planes of two octahedra in **2** have a dihedral angle of 115.7°. The average V═O and V−S distances are 1.60 and

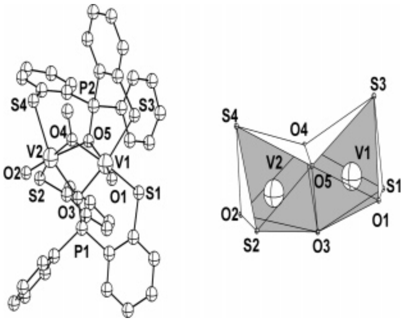

Figure 2. ORTEP diagram and polyhedral diagram of $\mathbf{2}\cdot H_2O$ shown with 35% thermal ellipsoids. H atoms, the anion, and the solvated H_2O molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): V1−O1 1.603(4), V1−O4 2.000(4), V1−O3 2.094(3), V1−O5 2.385(4), V1−S3 2.402(2), V1−S1 2.420(4), V1−V2 3.044(1), V2−O2 1.594(4), V2−O4 1.979(4), V2−O3 2.113(3), V2−O5 2.278(3), V2−S4 2.415(2), V2−S2 2.427(2); O1−V1−O5 170.7(2), O3−V1−S1 89.6(1), S1−V1−S3 83.28(6), S3−V1−O4 101.1(1), O4−V1−O3 77.3(1), S4−V2−S2 92.32(6), S2−V2−O3 92.3(1), O3−V2−O4 77.3(1), O4−V2−S4 91.7(1), O2−V2−O5 172.8(2).

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(12) Crystallographic data for **1**: $C_{66}H_{110}N_2O_4S_4Si_2V_2$, $M_r = 1281.91$; a green crystal (0.45 × 0.50 × 0.60 mm) sealed in a capillary with epoxy, $T = 200(2)$ K, λ(Mo Kα) = 0.710 73 Å, monoclinic, space group $P21/n$, $a = 17.2370(2)$ Å, $b = 24.1280(3)$ Å, $c = 17.7430(2)$ Å, $V = 7153.40(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.190$ g cm^{-3}, $2\theta_{max} = 50.16°$, $\mu = 0.455$ mm^{-1}, empirical absorption correction using *SADABS*, $F(000) = 2760$, 43 307 reflections, 12 368 unique reflections ($R_{int} = 0.0565$), 721 parameters, 0 restraint, GOF = 1.072, R1 = 0.0499 [$I > 2\sigma(I)$], wR2 = 0.1175, min/max residual electron density −0.482/0.686 e Å^{-3}, refined on $|F^2|$.

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(15) Crystallographic data for $\mathbf{2}\cdot H_2O$: $C_{53}H_{67}NO_6S_4P_2V_2$, $M_r = 1106.28$; a green crystal (0.30 × 0.40 × 0.45 mm) sealed in a capillary with epoxy, $T = 200(2)$ K, λ(Mo Kα) = 0.710 73 Å, monoclinic, space group $P21/n$, $a = 9.7871(4)$ Å, $b = 20.9209(10)$ Å, $c = 26.7300(14)$ Å, $V = 5436.2(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.355$ g cm^{-3}, $2\theta_{max} = 52.08°$, $\mu = 0.605$ mm^{-1}, empirical absorption correction using *SADABS*, $F(000) = 2332$, 23 194 reflections, 10 116 unique reflections ($R_{int} = 0.0651$), 613 parameters, 0 restraint, GOF = 1.170, R1 = 0.0772 [$I > 2\sigma(I)$], wR2 = 0.1881, min/max residual electron density −0.957/0.815 e Å^{-3}, refined on $|F^2|$.

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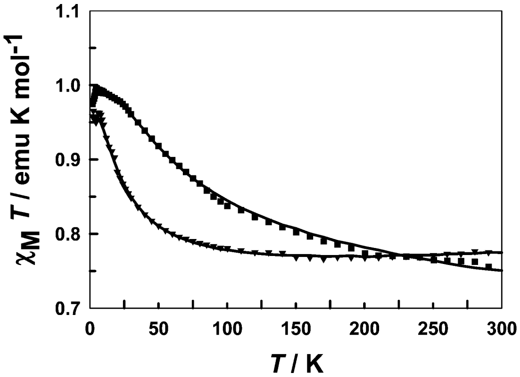

Figure 3. Temperature dependence of the magnetic susceptibility of compound **1** (squares) and compound **2** (triangles), in the form of $\chi_M T$, at 1 T. The solid lines represent the fitting results (see the text).

2.42 Å, respectively, comparable to those found in reported $V^{IV}{=}O$ and vanadium(IV) thiolate complexes.[9,14] The V−O(bridging phosphine oxide) distances are notably different; those trans to the terminal O are much longer than the others.

The magnetic data of **1** and **2** were measured with a SQUID magnetometer in a 1 T applied magnetic field and in the temperature range 2−300 K. The susceptibility data were corrected for diamagnetic contributions by using Pascal constants. The temperature dependences of $\chi_M T$ are shown in Figure 3. The $\chi_M T$ values at room temperature for **1** and **2** are 0.753 and 0.775 $cm^3\ mol^{-1}$ K, respectively, per binuclear molecule, which are closed to the spin-only value (0.75 $cm^3\ mol^{-1}$ K) for two uncoupled $S = {}^1/_2$ spins. They drastically increased with a decrease in the temperature to 0.996 and 0.958 $cm^3\ mol^{-1}$ K at 5.0 K for **1** and **2**, respectively. Such behaviors were in agreement with the presence of ferromagnetic ($S_T = 1$) interaction between the two V^{IV} ions. Below 5 K, the values slightly decreased, likely because of the zero-field-splitting or antiferromagnetic intermolecular interaction (Figure S1 in the Supporting Information). The susceptibility data were fitted to the van Vleck equation, a spin Hamiltonian of the form $H = -2JS_1 \cdot S_2$, with $S_1 = S_2 = {}^1/_2$. The satisfactory fits, as shown in Figure 3, give the following parameters: $g = 1.99$ and $J = 9.0\ cm^{-1}$ for **1** and $g = 1.96$ and $J = 3.2\ cm^{-1}$ for **2**. To confirm intramolecular ferromagnetic exchange interactions between two V^{IV} ions, the magnetization curves for **1** and **2** have been measured in the 0.1−7 T range and 2−5 K range (Figure S2 in the Supporting Information). The saturation values of 1.83 $N\beta$ for **1** and 1.84 $N\beta$ for **2** are close to the theoretical value of ca. 2 $N\beta$ expected for an $S_T = 1$ ground state.

Compounds **1** and **2** represent rare examples of dimeric oxovanadium(IV) complexes with a ferromagnetic interaction.[11a,18] Based on a qualitative explanation of the magnetic interactions, a direct overlap of d_{xy} orbitals (magnetic orbitals) is considered as the dominant antiferromagnetic exchange pathway for dinuclear oxovanadium(IV) complexes and ferromagnetic interactions are expected if two d_{xy} orbitals are orthogonal.[11a,19] Accordingly, the existing $[VO(\mu\text{-}OR)_2VO]^{2+}$ complexes (OR = phenoxo, alkoxo, and hydroxo bridging groups) with anti-coplanar and twist configurations have ferromagnetic interaction, while those with syn-orthogonal, anti-orthogonal, and syn-coplanar arrangements have antiferromagnetic interaction between two vanadyl centers.[11a] Compound **1** has the $[VO(\mu\text{-}OR)_2VO]^{2+}$ (OR = silanoxide) core unit in a syn-orthogonal arrangement but displays ferromagnetic coupling interaction between vanadyl ions. This unprecedented magnetostructural correlation appearing in **1** is likely due to the small dihedral angle (111.0°) between two basal planes, leading to the poor overlap of two d_{xy} orbitals and consequently resulting in the ferromagnetic coupling interaction between two vanadyl ions.[20] Compound **2** also exhibits intramolecular ferromagnetic exchange coupling between two vanadyl centers, again likely the result of a small dihedral angle (115.7°) between two equatorial planes in the structure. In addition, it should be highlighted that magnetic data have never been reported for dinuclear vanadium(IV) complexes with sulfhydryl groups as terminal ligands. How the S-terminal ligands in **1** and **2** versus N and O ligands appearing in other related examples facilitate the magnetic interaction between two vanadyl ions needs to be investigated further. Theoretical methods will be applied on these complexes to have a full understanding for the correlation between coupling constants and structural parameters as well as the coordination environment.

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Supporting Information Available: Synthetic procedures, characterizations, packing diagrams, and magnetization curves for **1** and **2**, and crystallographic data for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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