

Unprecedented $[V_2O]^{6+}$ Core of a Centrosymmetric Thiosemicarbazonato Dimer: Spontaneous Deoxygenation of Oxovanadium(IV)

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The complex cation $[V(dapts)(MeOH)]_2(\mu-O)]^{2+}$ [$dapts^{2-} = 2,6$ -diacetylpyridine bis(thiosemicarbazone)] is the first crystallographically elucidated dimer to possess a $[V_2O]^{6+}$ core, the $[V^{IV}-O-V^{IV}]^{6+}$ structural unit, formed by cleavage of the multiple bond in the oxo-cation VO^{2+} , is linear with the oxo group residing on a crystallographic center of inversion, and the temperature dependence of the magnetic data of the dimer is consistent with weak antiferromagnetic coupling of the d^1-d^1 centers.

Introduction

In recent years, much research effort has been devoted to exploring the potential of thiosemicarbazones and their complexes to exhibit biological activity (e.g., antibacterial, antimalarial, antiviral, and antitumor).¹ From a structural standpoint, the propensity of thiosemicarbazones to undergo tautomerism and form highly rigid, planar Schiff bases capable of imposing fascinating mixed-donor coordination environments about metal ions has stimulated widespread interest in this type of ligand.² Whereas there has been a preponderance of structurally characterized complexes of the tridentate ligands 2-formylpyridine thiosemicarbazone and 2-acetylpyridine thiosemicarbazone, the corresponding quinque-dentate ligand, 2,6-diacetylpyridine bis(thiosemicarbazone) (Figure 1), has received much less attention. Up until now, single-crystal X-ray analyses have been reported for a mere seven metal ions with the latter thiosemicarbazone,

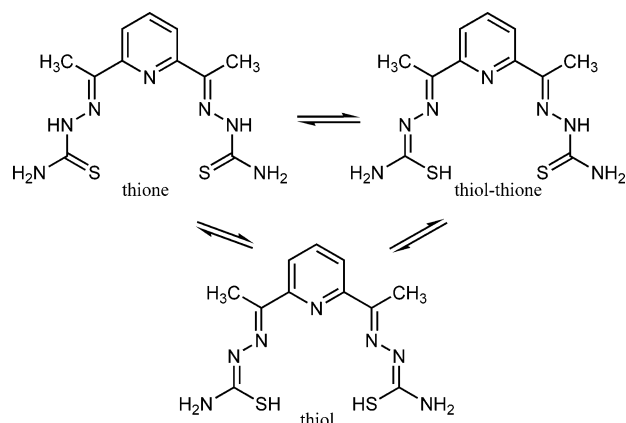


Figure 1. Metal-assisted in situ tautomerism of 2,6-diacetylpyridine bis(thiosemicarbazone) (H_2dapts).

viz., Fe(II),³ Mn(II),⁴ Zn(II),⁵ In(III),⁶ Tl(III),⁷ Bi(III),⁸ and Sn(IV).⁹ We are currently conducting a series of investiga-

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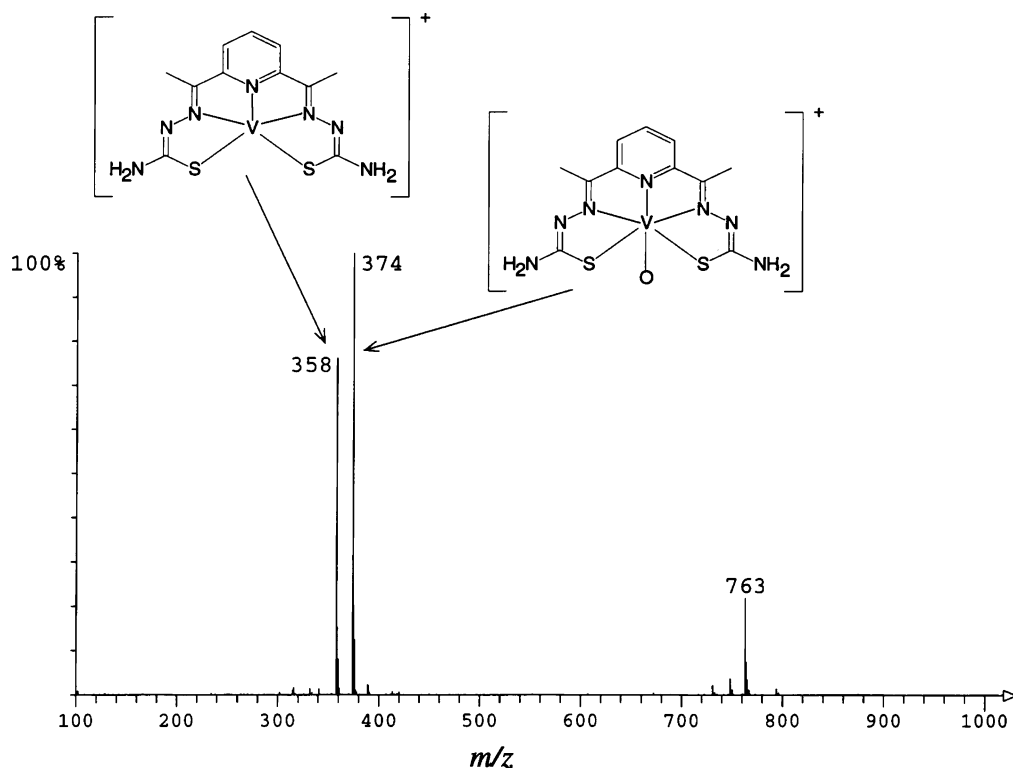


Figure 2. Positive-ion electrospray-ionization (ESI) mass spectrum of $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$.

tions of the reactivity of vanadium, particularly the VO^{2+} ion, with thiosemicarbazones of various denticities. The nature of the multiple bond in the vanadyl ion and the trans effect of the oxo group are of paramount interest to us. Further interest in this ion derives from the growing body of evidence that its complexes tend to exhibit pharmacological activity.¹⁰

Results and Discussion

Herein, we present the X-ray crystal structure of the dimeric vanadium(IV) compound $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$ and pertinent spectroscopic and magnetic features. The synthesis¹¹ of this compound involved reaction of VO^{2+} with an equivalent amount of the Schiff-base ligand 2,6-diacetylpyridine bis(thiosemicarbazone), H_2daptsc , in the presence of a 10-fold molar excess of ClO_4^- in refluxing methanol. Template reaction of stoichiometric amounts of 2,6-diacetylpyridine, thiosemicarbazide, and vanadyl sulfate

hydrate together with an excess of ClO_4^- afforded the same product. Although this dimeric compound is produced quite readily, occasionally its isolation in pure crystalline form is made difficult by the precipitation of trace amounts of an unidentified off-white byproduct. However, strategically, the desired product is obtained in pure form by filtering it off just before the impurity precipitates, but this causes low yields (20–41%).¹¹ Recrystallization is not an option since the vanadium compound never comes out of solution as crystals once dissolved. It is also noteworthy that the exclusion of perchlorate from the reaction leads to the formation of the monomer $[\text{VO}(\text{H}_2\text{daptsc})](\text{SO}_4)$.¹² The chemical composition of $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$ was verified by both microanalyses (C, H, N, S, and Cl)¹¹ and mass spectrometry. Figure 2 depicts the electrospray-ionization (ESI) mass spectrum of this compound obtained from blocks of crystals picked under the microscope. Although a peak corresponding to the dimeric complex cation (ESI positive-

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- (11) Synthesis and characterization of $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$: A mixture of H_2daptsc (0.1547 g, 0.50 mmol), $\text{VO}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ (0.1085 g, 0.50 mmol), and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (0.7023 g, 5.0 mmol) was suspended in methanol (25 mL) in a round-bottom flask. Upon being heated under reflux, a golden brown solution was formed and became progressively darker with time. After 20 min, the mixture was allowed to cool to room temperature and then filtered. The residue was discarded. The filtrate gave black rectangular blocks of crystals on slow evaporation of the solvent overnight. Prolonged periods of standing often resulted in precipitation of an impurity. $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$: Yield 0.1021 g (41.02%); Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{N}_{14}\text{O}_{11}\text{S}_4\text{V}_2$: C 28.95, H 3.44, Cl 7.12, N 19.69, S 12.88%; found: C 28.34, H 3.29, Cl 6.87, N 19.23, S 12.37%; ESI-MS: m/z : 763, 374, 358; IR (KBr)/ cm^{-1} (selected): 3434m, 3317m, 1621s, 1599s, 1557m, 1516vs, 1452s, 1354m, 1318m, 1287w, 1185m, 1171m, 1109vs, 1088vs, 1032m, 989m, 795m, 739m, 625 m, 483m.
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ion mode) was not detected, the fragmentation pattern revealed three structural constituents: $[\{V(\text{daptsc})\}_2(\text{MeOH})(\mu\text{-O})]^+$ ($m/z = 763$, indicative of loss of one of the two methanol solvent molecules), $[V(\text{daptsc})\text{O}]^+$ ($m/z = 374$), and $[V(\text{daptsc})]^+$ ($m/z = 358$).

The conversion of the tautomeric forms of H_2daptsc in the aforementioned reaction was monitored by IR spectroscopy. The vibrations of the amine groups of the uncoordinated ligand H_2daptsc (thione form) are characterized by absorption bands at 3424, 3260 [$\nu(\text{NH}_2)$], and 3166 cm^{-1} [$\nu(\text{NH})$]. However, the absorption band associated with $\nu(\text{NH})$ is conspicuous by its absence from the IR spectrum of $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$; neither is a $\nu(\text{SH})$ band present, pointing to in situ tautomerism of H_2daptsc with subsequent deprotonation to afford daptsc^{2-} in the thiolate form (Figure 1). Indeed, the IR spectrum of the ligand displayed two of the thione $\text{C}=\text{S}$ stretching frequencies at 874 and 809 cm^{-1} , whereas that of the vanadium dimer exhibited corresponding absorptions of the thiolate $\text{C}-\text{S}$ vibrations at comparatively lower energies (795 and 739 cm^{-1}). Prior to the structure determination of this compound, the existence of the uncoordinated perchlorate counterions was recognized by the characteristic vibrational bands of these ions.^{11,13}

The compound $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$ crystallizes from a methanol solution under ambient conditions in the monoclinic system, space group $P2_1/c$.¹⁴ The X-ray crystal structure consists of an oxo-bridged dimeric vanadium complex cation with two disordered perchlorate counterions. The complex cation (Figure 3) displays C_i symmetry with the oxo bridge lying on the crystallographically imposed center of symmetry. The geometry about each of the vanadium atoms can be described as distorted pentagonal bipyramidal with the donor atoms of the planar quinque-dentate thiosemicarbazonato ligand coordinating equatorially whereas the bridging oxygen atom and the oxygen of a methanol solvent molecule occupy the axial positions. Heptacoordinate Schiff-base complexes of vanadium are extremely rare.¹⁵ The distortion of the geometry at the

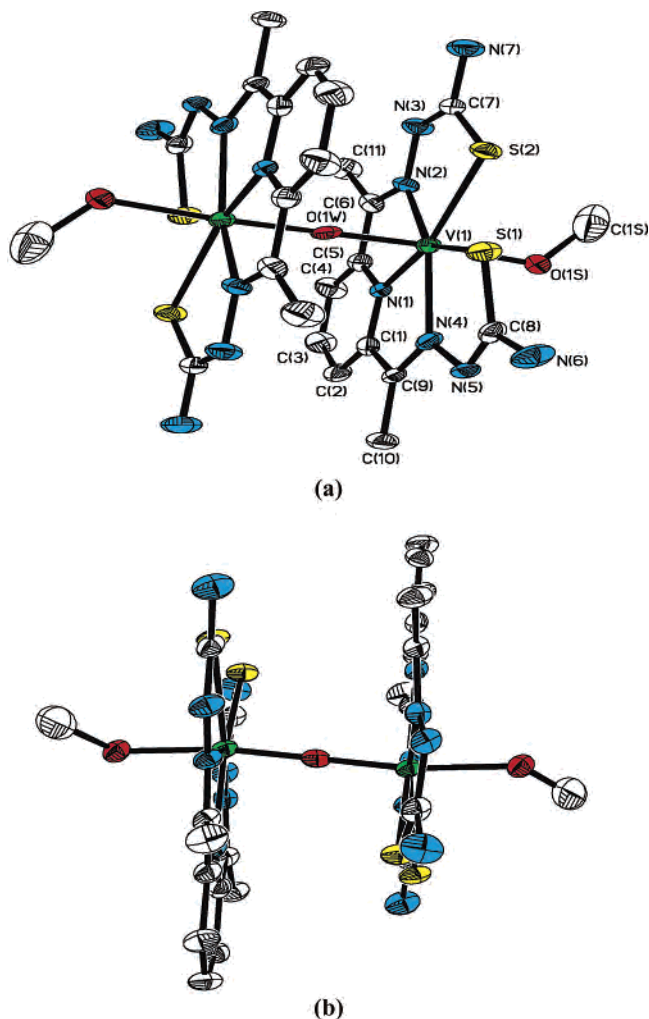


Figure 3. ORTEP diagrams of the dimeric complex cation $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})]^{2+}$ with thermal ellipsoids at the 50% probability level: (a) top view and (b) side view.

Table 1. Selected Bond Distances (Å) and Angles (deg) in $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})]^{2+}$

V(1)–O(1W)	1.7605(10)	V(1)–N(4)	2.202(4)
V(1)–O(1S)	2.076(4)	V(1)–S(2)	2.4259(16)
V(1)–N(1)	2.110(4)	V(1)–S(1)	2.4469(17)
V(1)–N(2)	2.198(5)		
V(1)#–O(1W)–V(1)	180.00(8)	O(1W)–V(1)–N(2)	86.66(12)
S(2)–V(1)–S(1)	67.30(5)	O(1S)–V(1)–N(2)	89.06(16)
N(1)–V(1)–N(4)	72.36(16)	O(1W)–V(1)–N(4)	95.33(12)
N(1)–V(1)–N(2)	72.24(16)	O(1S)–V(1)–N(4)	83.87(15)
N(2)–V(1)–S(2)	74.62(12)	O(1W)–V(1)–S(2)	97.23(5)
N(4)–V(1)–S(1)	73.85(12)	O(1S)–V(1)–S(2)	88.75(11)
O(1W)–V(1)–O(1S)	171.46(11)	O(1W)–V(1)–S(1)	93.75(6)
O(1S)–V(1)–N(1)	85.16(16)	O(1S)–V(1)–S(1)	94.19(12)
O(1W)–V(1)–N(1)	86.49(12)		

vanadium center, evidenced by the deviations from the idealized angles 72°, 90°, and 180°, as well as the considerable differences in the bond distances in the coordination sphere, is a consequence of ligand constraints (Table 1).

That the vanadium atoms are in the tetravalent state ($[\text{Ar}]-3d^1$) is inferred from the crystallographically determined formulation $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$ and ascertained from magnetic studies. The dimerization of the vanadium(IV) complex evidently by cleavage of the multiple bond in the highly stable VO^{2+} ion was unexpected.

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(14) Crystal data for $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$: $\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{N}_{14}\text{O}_{11}\text{S}_4\text{V}_2$, $M = 995.67$, crystal dimensions $0.32 \times 0.21 \times 0.12 \text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 9.286(3) \text{ \AA}$, $b = 9.478(3) \text{ \AA}$, $c = 21.541(6) \text{ \AA}$, $\beta = 96.008(5)^\circ$, $U = 1885.5(9) \text{ \AA}^3$, $Z = 2$, $D_c = 1.754 \text{ Mg/m}^3$, $\mu(\text{Mo K}\alpha) = 0.935 \text{ mm}^{-1}$. The data were recorded at 150(2) K on a Bruker SMART CCD area detector [$\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$] with Oxford Cryosystems low-temperature system. Cell parameters were refined from the setting angles of 24 reflections (θ range 1.90–28.32°). Of the 11 759 reflections measured, 4499 were independent ($R_{\text{int}} = 0.0963$). The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for Me groups) and with U_{iso} constrained to be 1.2 (1.5 for Me groups) times U_{eq} of the carrier atom. The perchlorate ions are disordered. Atoms O(4A), O(4B), O(1A), and O(1B) were refined anisotropically to an occupancy of 63:37. Refinement converged at a final $R1 = 0.0738$, $wR2 = 0.1705$ [$I > 2\sigma(I)$].

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Deoxygenation of VO^{2+} is usually effected with reagents such as SOCl_2 , SOBr_2 , PCl_5 , RCOX ($X = \text{Cl}, \text{Br}$), SeOCl_2 , COCl_2 , and HX ($X = \text{Cl}, \text{Br}$).^{15,16} Not only is $[\{\text{V}(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})]^{2+}$ the first example of a crystallographically characterized complex of vanadium(IV) with a thiosemicarbazato ligand derived from unsubstituted thiosemicarbazide, but it also represents the first structurally characterized dimer to possess the $[\text{V}_2\text{O}]^{6+}$ core. The bridging unit $[\text{V}^{\text{IV}}\text{-O}-\text{V}^{\text{IV}}]^{6+}$ is linear ($\text{V}-\text{O}-\text{V} = 180^\circ$). The $\text{V}^{\text{IV}}\text{-O}_{\mu\text{-oxo}}$ bond $[\text{V}(1)\text{-O}(1\text{W}) = 1.7605(10) \text{ \AA}]$ in this dinuclear cation is significantly longer than the vanadyl $\text{V}=\text{O}$ bond (1.57–1.61 \AA) commonly observed in mononuclear complexes of oxovanadium(IV),^{15,17} but nevertheless still demonstrates considerable multiple-bond character ($d_\pi\text{-p}_\pi$ interaction) whose trans effect manifests itself in the weak coordination of the methanol solvent molecules in the trans positions. Dimers containing the structural unit $[\text{V}^{\text{III}}\text{-O}-\text{V}^{\text{III}}]^{4+}$ arising from the hydrolysis of V(III) are quite common.¹⁸ There is also a growing number of vanadium dimers which possess the mixed-valence bridging unit $[\text{OV}^{\text{IV}}\text{-O}-\text{V}^{\text{V}}\text{O}]^{3+}$.¹⁹ However, dinuclear complexes of vanadium with the cores $[\text{OV}^{\text{IV}}\text{-O}-\text{V}^{\text{IV}}\text{O}]^{2+}$ ²⁰ and $[\text{OV}^{\text{V}}\text{-O}-\text{V}^{\text{V}}\text{O}]^{4+21}$ are rare.

X-ray crystallography has provided definitive evidence for the in situ conversion of the thiosemicarbazone ligand from the thione tautomer to the thiolate form (Figure 1). The Schiff-base $\text{C}=\text{N}$ bonds $[\text{N}(2)\text{-C}(6) = 1.292(7) \text{ \AA}]$ and $[\text{N}(4)\text{-C}(9) = 1.300(6) \text{ \AA}]$ are equidistant with the $\text{C}=\text{N}$ bonds of the pendant thiosemicarbazato units $[\text{N}(3)\text{-C}(7) = 1.306(7) \text{ \AA}]$ and $[\text{N}(5)\text{-C}(8) = 1.302(7) \text{ \AA}]$. The $\text{C}-\text{S}$ bond distances $[\text{S}(1)\text{-C}(8) = 1.719(5) \text{ \AA}]$ and $[\text{S}(2)\text{-C}(7) = 1.738(6) \text{ \AA}]$ are consistent with the existence of thiolate bonds ($\text{C}-\text{S}^-$) rather than thione bonds ($\text{C}=\text{S}$) which are $\sim 1.68 \text{ \AA}$ long.⁶ Interestingly, in some of the reported complexes of 2,6-diacetylpyridine bis(thiosemicarbazone), the ligand is singly deprotonated, i.e., one pendant arm exists in the thione form while the other exists in the thiolate form.^{5-7,9}

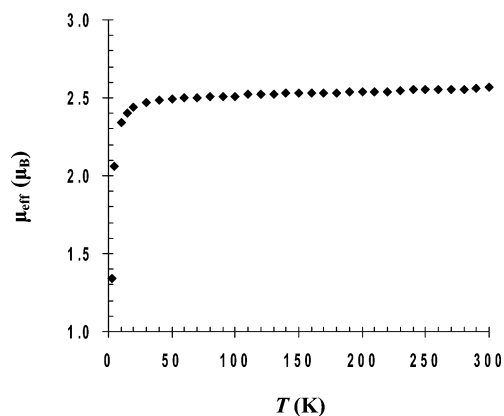


Figure 4. 4. Variation of effective magnetic moments (μ_{eff}) of $[\{\text{V}(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$ with temperature.

Variable-temperature magnetic susceptibility measurements of $[\{\text{V}(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$ were carried out on a SQUID magnetometer in the range 2–300 K, and diamagnetic corrections were performed the usual way using Pascal's constants. A plot of the effective magnetic moments (μ_{eff}) as a function of absolute temperature is given in Figure 4. The room-temperature experimental value of the effective magnetic moment ($\mu_{\text{eff}} = 2.55 \mu_B$; $\chi_M T = 0.813 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) is comparable with the spin-only value of $2.45 \mu_B$ ($\chi_M T = 0.750 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$; $\mu_{\text{eff}} = g[S_1(S_1 + 1) + S_2(S_2 + 1)]^{1/2}$, $g = 2.0$) expected for two uncoupled paramagnetic centers each with $S = 1/2$. These magnetic measurements corroborate the crystallographic analysis that pointed to a tetravalent state for each of the oxo-bridged vanadium atoms. There is a steady decrease in the magnetic moments of the $\text{V}(\text{IV})\text{-O}-\text{V}(\text{IV})$ dimer from room temperature to about 50 K in conformity with the Curie–Weiss law [$\chi_M = C/(T - \theta)$]. Below 50 K, there is deviation from linearity with a sharp drop in μ_{eff} from 10 to 2 K [$2.34 \mu_B$ ($\chi_M T = 0.684 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) at 10 K and $1.34 \mu_B$ ($\chi_M T = 0.224 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) at 2 K]. This magnetic behavior is consistent with antiferromagnetic coupling of the $d^1\text{-}d^1$ metal centers. Fitting of the magnetic data to the expression for χ_M vs T derived from the spin-exchange Hamiltonian $H = -2JS_1S_2$ ($S_1 = S_2 = 1/2$) gave the value of the exchange coupling parameter as -1.6 cm^{-1} . Details of the analysis of the magnetic data of $[\{\text{V}(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$ along with those of other related vanadium complexes will be presented elsewhere.

The X-band EPR powder spectrum of $[\{\text{V}(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$ ($I = 7/2$ for ^{51}V) recorded at 80 K (using a frequency of 9.43 GHz, a microwave power of 40 mW, a modulation frequency of 100 kHz, and a modulation amplitude of 2 mT) is consistent with a $d^1\text{-}d^1$ dimeric low-lying triplet ($S = 1$) state.²² The spectrum exhibits resonances

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Spontaneous Deoxygenation of Oxovanadium(IV)

in the range 280–410 mT, corresponding to $\Delta M_s = \pm 1$ absorptions, and a signal centered around 165 mT with a relatively lower intensity. This weak absorption in the “half-field” region is particularly important because it is readily associated with the $\Delta M_s = \pm 2$ transition which violates the spin selection rule ($\Delta M_s = \pm 1$).²² Traces of a paramagnetic monomeric species with $S = 1/2$ were indicated by a weak absorption around 340 mT. Indeed, in previous studies of dinuclear oxovanadium(IV) complexes, such an impurity was detected by ESR spectroscopy.^{22d–f} As observed in related dinuclear vanadium systems, it is difficult to remove this paramagnetic impurity completely if the samples of the desired dimers cannot be recrystallized.^{19b}

The black crystals of $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$ dissolve readily in DMSO but slowly in methanol or water to give intense golden brown solutions. The electronic spectrum of the dimer was recorded in methanol in the range 190–1110 nm. Intraligand absorptions were observed at 220, 265, and 290 nm. The visible absorptions at 355, 540, 790, and 895 nm—none of which is observed in the electronic spectrum of the colorless uncoordinated ligand, H_2daptsc —

are responsible for the color of the complex. The origin and nature of the electronic transitions (LMCT and ligand-field) associated with the visible bands will be determined once it has been ascertained whether the dimer remains intact in solution. For instance, the complex $[\text{Et}_3\text{NH}]_2[\text{O}=\text{V}(\text{BBAC})_2]$ [$\text{H}_3\text{BBAC} = N,N$ -bis(2-hydroxybenzyl)aminoacetic acid]^{22d} has been shown through systematic spectroscopic studies to undergo dissociation into the corresponding monomer in solution.

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Supporting Information Available: Crystallographic information file (CIF) for $[\{V(\text{daptsc})(\text{MeOH})\}_2(\mu\text{-O})](\text{ClO}_4)_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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