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The First Oxovanadium(V)−Thiolate Complex, $[VO(SCH_2CH_2)_3N]$

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The chemistry of vanadium bound to sulfur donor ligands has drawn considerable attention because of its relevance to several biological[1] and industrial processes, for example, conducting vanadium−sulfur materials,[2] extraction of vanadium impurities from the heavier crude oils,[3] and use of $V^{IV}O$ and $V^{V}O$ complexes[4] as catalysts for the conversion of sulfides to sulfoxides. Vanadate, which acts as an inhibitor[5] toward a number of enzymes, such as ATP phosphohydrolases, ribonuclease, and phosphotyrosyl protein phosphatase, undergoes intracellular reduction to vanadyl (VO^{2+}) by NADH, ascorbate or glutathione. An EPR study[6] of the entry of vanadate ions into rat adipocytes confirmed formation of VO^{2+} and showed that it forms a 1:1 complex with reduced glutathione (GSH). Experimental evidence is yet to be presented for the kinetic mechanism of *in vivo* or *in vitro* reduction of VO_4^{3-} to VO^{2+} by thiols. Nonetheless, mechanistic studies[7,8] of the analogous reduction of Cr(VI) by glutathione, cysteine, cysteamine, mercaptoethanol, or penicillamine at physiological pH revealed initial Cr(VI)−thiolate formation. Against this background, interaction of VO^{3+} with thiolate appears to be important. Although several V^{3+},[9] V^{4+},[10] and VO^{2+} [10a,11] complexes of thiolate are structurally characterized, no VO^{3+}−thiolate complex has been reported so far. The only structure available for a V(V)−thiolate complex[12] contains a non-oxovanadium−thiophenolate bond. We report here the synthesis, characterization and structure of the first oxovanadium(V)−thiolate complex, $[VO(SCH_2CH_2)_3N]$ (**1**).

Compound **1** was prepared by stirring an ethanol solution of trithiatren[13] and $VO(OEt)_3$[14] in equimolar quantities at room temperature for 1 h. The precipitated red solid was recrystallized from warm acetonitrile/methanol as dark red needles[15] (yield 80%). It can also be prepared from $VO(acac)_2$ in 60% yield. Single crystals[16] were obtained by diffusing diethyl ether into an acetonitrile solution of the compound.

Figure 1 shows the ORTEP plot of **1**. The molecule has noncrystallographic pseudo-3-fold rotation symmetry with the V−N bond as the axis. The geometry around the vanadium

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(1) (a) Chasteen, N. D., Ed. *Vanadium in Biological Systems*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1990. (b) Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 148. (c) Butler, A.; Walker, J. V. *Chem. Rev.* **1993**, *93*, 1937.

(2) Rouxel, J.; Brec, R. *Annu. Rev. Mater. Sci.* **1986**, *16*, 137.

(3) Reynolds, J. F.; Biggs, W. R.; Fetzer, J. C. *Liq. Fuel Technol.* **1985**, *3*, 423.

(4) (a) Nakajima, K.; Kojima, K.; Kojima, M.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2620. (b) Nakajima, K.; Kojima, M.; Toriumi, K.; Saito, K.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 760.

(5) Nechay, B. R. *Annu. Rev. Pharmacol.* **1984**, *24*, 501.

(6) Degani, H.; Gochin, M.; Karlish, S. J. D.; Schechter, Y. *Biochemistry* **1981**, *20*, 5795.

(7) Connett, P. H.; Wetterhahn, K. E. *J. Am. Chem. Soc.* **1985**, *107*, 4282.

(8) (a) McAuley, A.; Olatunji, M. A. *Can. J. Chem.* **1977**, *55*, 3335. (b) O'Brien, P.; Ozolins, Z. *Inorg. Chim. Acta* **1989**, *161*, 261.

(9) (a) Szeymies, D.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 885. (b) Kawaguchi, H.; Tatsumi, K.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1995**, 111.

(10) (a) Christou, G.; Heinrich, D.; Money, J. K.; Rambo, J. R.; Huffman, J. C.; Folting, K. *Polyhedron* **1989**, *8*, 1723. (b) Money, J. K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1988**, *27*, 507.

(11) Tsagkalidis, W.; Rodewald, D.; Rehder, D. *Inorg. Chem.* **1995**, *34*, 1943.

(12) Money, J. K.; Nicholson, J. R.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4072.

(13) Barbaro, P.; Bianchini, C.; Scapacci, G.; Masi, D.; Zanello, P. *Inorg. Chem.* **1994**, *33*, 3180.

(14) Cornman, C. R.; Kampf, J.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1992**, *31*, 2035.

(15) IR (KBr): 973 cm^{-1} ($\nu_{V=O}$). UV−vis (dimethylformamide), λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 500 (8250), 375 (7210). ^1H NMR: δ (DMSO-d_6) 3.45 (2H, triplet), 3.89 (2H, triplet). Anal. Calcd for $C_6H_{12}NOS_3V$: C, 27.6; H, 4.59; N, 5.37. Found: C, 27.7; H, 4.58; N, 5.29.

(16) Crystal data for **1**: dark red prism, formula = $C_6H_{12}NOS_3V$, fw = 261.29, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.522(3)$ Å, $b = 10.520(3)$ Å, $c = 7.237(2)$ Å, $\alpha = 90.59(2)°$, $\beta = 112.84(2)°$, $\gamma = 100.86(3)°$, $V = 516.1(6)$ Å^3, $Z = 2$. Single crystal diffraction data for **1** were collected on a Rigaku AFC6S diffractometer using the ω-2θ scan technique to a maximum 2θ value of 53.1°, with graphite-monochromated Mo Kα ($\lambda = 0.710\ 69$ Å) radiation at 25 °C. Scans of $(1.68 + 0.30 \tan \theta)°$ were made at a speed of 4.0° min^{-1} (in ω) to include $0 \le h \le +9$, $-13 \le k \le +13$, $-9 \le l \le +9$. Of the 2319 collected reflections, 2151 were unique ($R_{int} = 0.039$); equivalent reflections were merged. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1110 observed reflections ($I > 3\sigma_I$) and 109 variable parameters and converged with $R = 0.038$ and $R_w = 0.038$. At the final stage of refinement, the difference map showed minimum and maximum peaks between −0.48 and +0.65 e Å^{-3}.

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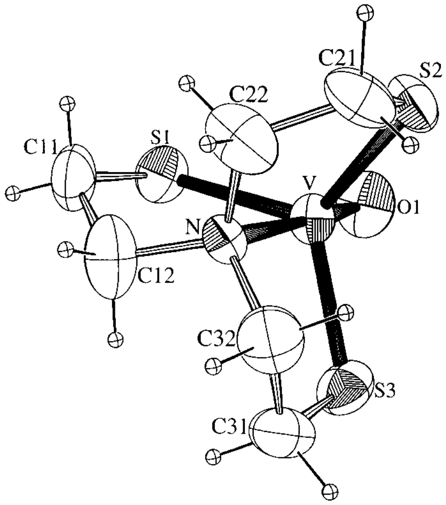

Figure 1. ORTEP drawing for $[VO(SCH_2CH_2)_3N]$. Selected bond distances (Å) and angles (deg): V−S(1) = 2.249(3), V−S(2) = 2.247(3), V−S(3) = 2.242(3), V−O(1) = 1.578(6), V−N = 2.291(6); S(1)−V−S(2) = 119.8(1), S(1)−V−S(3) = 118.1(1), S(2)−V−S(3) = 118.0(1), N−V−O(1) = 178.6(3), S(1)−V−N = 82.9(2), S(2)−V−N = 83.0(2), S(3)−V−N = 83.6(2), S(1)−V−O(1) = 96.6(2), S(2)−V−O(1) = 96.1(2), S(3)−V−O(1) = 97.8(3).

atom is a slightly distorted trigonal bipyramid, with thiolate sulfurs occupying the equatorial positions. The vanadium atom is pulled out of the equatorial plane toward the doubly bonded oxygen atom by 0.267 Å. The V−N bond length (2.291(6) Å) is somewhat longer than that found in the trigonal bipyramidal oxovanadium(V) triethanolaminate complexes[17] (2.276 Å) but similar to the $N-V^VO$ distance (2.313 Å) in [VO(Salshedr)][19d] and even to the V−N bond length (2.297 Å) in the mixed-valence $[V_2O_3(Nta)_2]^{3-}$.[18] Compared to those for the triethanolaminate analogue, the slightly larger S−V−N angles may be viewed as a mechanical consequence of the greater radius of the sulfur donor atoms. Although the observed V−O distance (1.578(6) Å) is shorter than that in the triethanolaminate (1.633 Å) or tris(2-propanol)aminate (1.794 Å) complexes,[17] it is nonetheless comparable with those of several other oxovanadium(V) complexes.[19] The V−S(thiolate) bond lengths are shorter than in $[VS_2(S_2)(SPh)]$ (2.361 Å).[12]

The electronic spectrum of EPR-silent **1** (Figure 2) in dimethylformamide exhibits two strong thiolate-to-vanadium charge-transfer transitions, at 500 and 375 nm, assignable as arising from thiolate S_π and S_σ ground states, respectively.[20] Moreover, the insensitivity of the absorption spectrum to solvent (dimethylformamide *vs* MeOH *vs* $MeNO_2$) evidences retention of the solid state structure in solution. Cyclic voltammetry[21] of **1** in dimethylformamide shows that reduction of $[VO(SCH_2CH_2)_3N]$ to $[VO(SCH_2CH_2)_3N]^-$ takes place quasireversibly at −1.15 V *vs* $Ag/Ag(ClO_4)$. This relatively cathodic value and the absence of any further reductions above − 2.5 V emphasize the relative stabilization of trigonal V(V) afforded by tripodal ligands and of such higher oxidation states by the anionic charge of thiolate.[22]

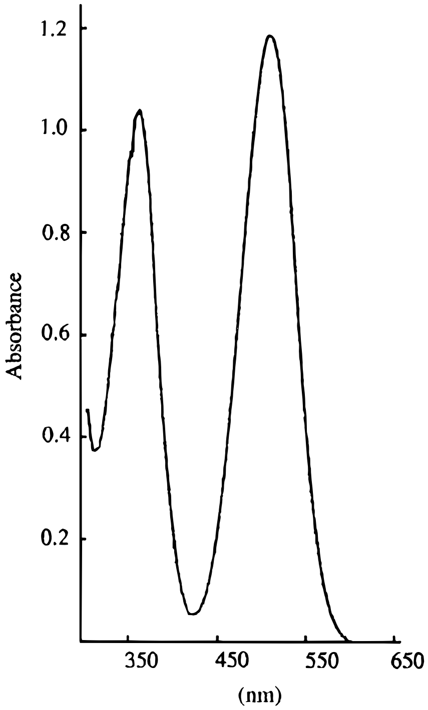

Figure 2. Electronic absorption spectrum of $[VO(SCH_2CH_2)_3N]$ (1.442×10^{-4} M) in dimethylformamide.

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Supporting Information Available: Tables of crystal data and refinement details, atomic coordinates and thermal parameters, anisotropic thermal parameters, complete bond distances and angles, and least-squares planes and a unit cell stereoview for **1** (7 pages). Ordering information is given on any current masthead page. These data may be available from the author on the Internet at http://129.25.1.71/chemistry/research/newmolecules/metals/vanadium.html.

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(17) Crans, D. C.; Chen, H.; Anderson, O. P.; Miller, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 6769.

(18) Nishizawa, M.; Hirotsu, K.; Ooi, S.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1979**, 707. Nta is the nitrilotriacetate trianion.

(19) (a) Scheidt, W. R. *Inorg. Chem.* **1973**, *12*, 1758. (b) Bonadies, A. J.; Butler, W. M.; Pecoraro, V. L.; Carrano, C. J. *Inorg. Chem.* **1987**, *26*, 1218. (c) Fischer, D. C.; Barclay-Peet, S. J.; Balfe, C. A.; Raymond, K. N. *Inorg. Chem.* **1989**, *28*, 4399. (d) Colpas, G. J.; Hamstra, B. J.; Kampf, J. W.; Pecoraro, V. L. *Inorg. Chem.* **1994**, *33*, 4669.

(20) McMillin, D. R.; Morris, M. C. *Proc. Natl. Acad Sci. U.S.A.* **1981**, *78*, 6567. the possibility that the two bands arise from the inaccessibility of 3-fold degeneracy for the S_σ orbitals cannot be discarded.

(21) Cyclic voltammetry was performed as previously described[22] in oxygen-free dimethylformamide with 0.1 M NEt_4ClO_4 supporting electrolyte, platinum working and auxiliary electrodes, and an Ag^+ (0.01 M, 0.1 M NEt_4ClO_4, CH_3CN)/Ag reference electrode (+0.077 V in CH_3CN for ferrocenium/ferrocene) at 50 mV s^{-1} scan rate.

(22) Addison, A. W.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1984**, *23*, 1957.