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Structure and Solution Properties of a Dimeric Tetrahedral Vanadium(V) Chloride Alkoxide Complex

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Although the literature is now replete with a number of structurally characterized oxovanadium(V) derivatives containing organic ligands,[1] only three compounds: two vanadium(V) siloxides[2] and one vanadium(V) chloride diaryloxide, $VOCl(ULTRA)$ ($ULTRA = 2,2'\text{-}CH_2(4\text{-}CH_3\text{-}6\text{-}C(CH_3)_3C_6H_2O)_2$),[3] contain tetrahedrally coordinated oxovanadium(V). Structural characterization of oxovanadium(V) alkoxides show such compounds have coordination numbers greater than 4. In the solid state, $VO(OCH_3)_3$ is polymeric; each vanadium atom has a coordination sphere containing six ligands as a result of bridging alkoxide groups.[4] The compounds $VO(OCH_2CH_2Cl)_3$[5] and $VO(\textit{cyclo}\text{-}C_5H_9O)_3$[6] also contain loosely bridging alkoxide ligands to form five-coordinate dimeric complexes. Recently we reported the structure of a five-coordinate oxovanadium(V) chloride dialkoxide compound with a 1,2-diol ligand $[VOCl(OC(CH_3)_2C(CH_3)_2O)]_2$.[7] The halves of the dimer are related by a center of inversion with one oxygen of each alkoxide pinacol moiety bridging between vanadium atoms. The formation of dimers due to alkoxide, aryloxide, or oxide bridges is a common feature in oxovanadium(III), -(IV), and -(V) compounds.[4-8] In contrast, the exact nature of the bridging of 1,2-diols in aqueous complexes of vanadium(V) nucleosides is less well characterized and evidence for alternative bridging structures has been presented.[9] The bridging of alkoxo oxygen atoms in vicinal diols to form five-coordinate vanadium dimers is not the only possibility, although no other structural characterization of such compounds has been reported. We have found that an alternative mode of bridging in a dinuclear vanadium(V) complex results when ethylene glycol is used as a 1,2-diol ligand. Herein we report the preparation and characterization of this first tetrahedrally coordinated dimeric oxovanadium(V) chloride alkoxide compound.

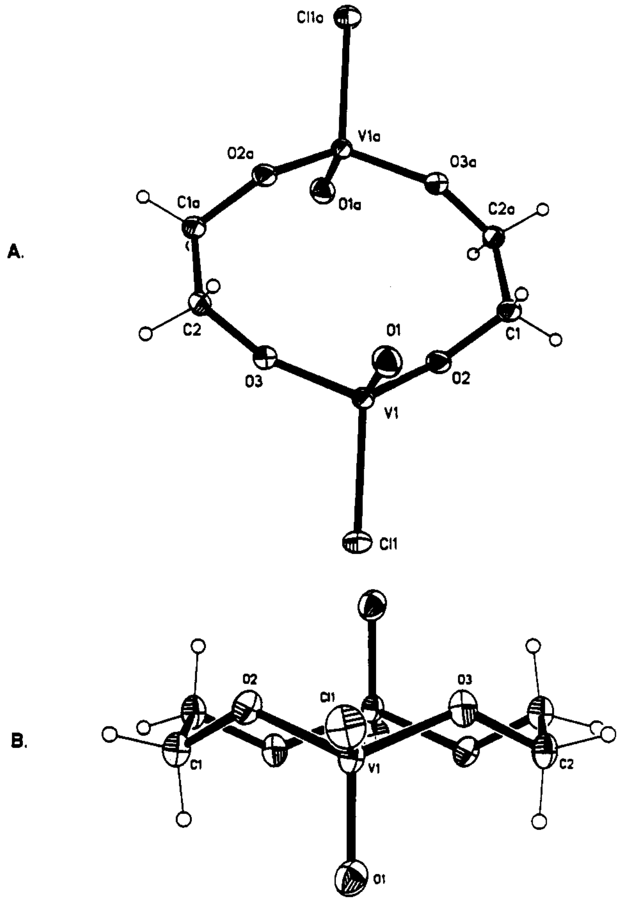

Figure 1. (A) ORTEP drawing of **1**. Selected bond distances (Å) and angles (deg): V1–Cl1 = 2.207 (1), V1–O1 = 1.578 (2), V1–O2 = 1.741 (2), V1–O3 = 1.743 (2), O2–C1 = 1.422 (2), O3–C2 = 1.433 (3), C1–C2a = 1.505 (3); Cl1–V1–O1 = 108.3 (1), Cl1–V1–O2 = 113.0 (1), O1–V1–O2 = 107.1 (1), Cl1–V1–O3 = 110.2 (1), O1–V1–O3 = 107.9 (1), O2–V1–O3 = 110.2 (1), V1–O2–C1 = 134.0 (2), V1–O3–C2 = 135.3 (2). (B) Side view of **1**.

Under an atmosphere of dry argon, dropwise addition of $VOCl_3$ (0.92 g, 5.3 mmol) to a CH_2Cl_2 solution of 1,2-bis(trimethylsiloxy)ethane (1.1 g, 5.3 mmol) at –60 °C in the dark produced a dark red solution. The temperature of the solution was raised to 25 °C, and the solution was stirred for 12 h. During that time, a white solid precipitated from solution. The solid was isolated by filtration and redissolved in 10% (v/v) hexane/CH_2Cl_2 solution; the resultant mixture was then allowed to cool in a freezer at –20 °C overnight. Colorless crystals of $[VOCl(OCH_2CH_2O)]_2$ (**1**) were obtained in 60% yield.[10,11] ORTEP drawings of **1** are shown in Figure 1, and selected bond lengths and angles are given in the caption. Figure 1B is a side view of the ten-membered ring showing the conformation of the ring and the location of the Cl and oxo substituents. The geometry about each of the vanadium atoms is a slightly distorted tetrahedron with one oxo ligand, two alkoxide oxygen atoms, and a chloro ligand. The bond angles between the atoms attached to the vanadium center are within 4° of idealized tetrahedral angles. The bond lengths of V═O and V—Cl are 1.578 (2) and 2.207 (1) Å, respectively, which compare well to those observed for the pinacol dimer (1.576 (1) and 2.219 (1) Å). The lengths of the V—O bonds (1.741 (2) and 1.743 (2) Å) are 0.03 and 0.22 Å shorter than those observed for the pinacol dimer. These differences are not surprising given the greater strain and pentacoordination in the pinacol dimer. Much smaller differences are observed when the bond lengths of **1** are compared with those of $VO(OSiPh_3)_3$ (1.743 (2), 1.745 (2), and 1.739 (3) Å) and $VOCl(ULTRA)$ (1.752 (4) and 1.734 (3) Å), indicating that the bond lengths of **1** fall within the range of expected values according to previously reported results for vanadium(V) compounds with ligands in a tetrahedral geometry.

Although a tetrahedral array of ligands about the vanadium(V) center was suspected on the basis of the ^{51}V NMR chemical shift, the dinuclear structure with tetrahedral vanadium(V) centers was not anticipated. A mononuclear complex would have

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(1) Recent reviews: (a) Chen, Q.; Zubieta, J. *Coord. Chem. Rev.* **1992,** *114,* 107. (b) Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 148. (c) Klemperer, W. G.; Marquart, T. A.; Yaghi, O. M. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 49.

(2) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1991,** *30,* 1689.

(3) Toscano, P. J.; Schermerhorn, E. J.; Dettelbacher, C.; Macherone, D.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1991,** 933.

(4) Cauglin, C. N.; Smith, H. M.; Watenpaugh, K. *Inorg. Chem.* **1966,** *5,* 2131.

(5) Preibsch, W.; Rehder, D. *Inorg. Chem.* **1990,** *29,* 3013.

(6) Hillerns, F.; Olbrich, F.; Behrens, U.; Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 447.

(7) Crans, D. C.; Felty, R. A.; Miller, M. M. *J. Am. Chem. Soc.* **1991,** *113,* 265.

(8) (a) Hambley, T. W.; Judd, R. J.; Lay, P. A. *Inorg. Chem.,* **1992,** *31,* 345. (b) Bottomley, F.; Magill, C. P.; White, P. S. *J. Am. Chem. Soc.* **1989,** *111,* 3070. (c) Djordjevic, C.; Lee, M.; Sinn, E. *Inorg. Chem.* **1989,** *28,* 719. (d) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.,* **1983,** *22,* 378. (e) Gambarotta, S.; Bolhuis, F. V.; Chiang, M. Y. *Inorg. Chem.* **1987,** *26,* 4303. (f) Mazzanti, M.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1989,** 1793.

(9) Crans, D. C.; Harnung, S. E.; Larsen, E.; Shin, P. K.; Theisen, L. A.; Trabjerg, I. *Acta Chem. Scand.* **1991,** *45,* 456.

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contained tetrahedral vanadium; however, geometrically nonrestricted bidentate diols do not readily form mononuclear compounds, despite efforts to generate these.[5,12,13] Nevertheless, it is surprising that the ethylene glycol forms a ten-membered ring in a binuclear complex rather than a five-membered ring in a mononuclear complex. X-ray crystallographic studies of vanadate bound to uridine inside ribonuclease A have shown a five-membered ring in a mononuclear complex.[14] Also, five-membered-ring containing products are thought to form between vanadate and various diols in aqueous solution.[15] Despite these findings, MCD and CD spectroscopic studies of aqueous solutions do not support a five-membered ring in the major vanadate–nucleoside complex, but rather suggest alternative structures in which the diol bridges across two vanadium centers similar to that observed in **1**.[9] The previously characterized pinacol complex is also dinuclear; however, the vanadium is pentacoordinate because one of the alkoxide oxygen atoms bridges between the two vanadium atoms present in this complex, forming an internal four-membered ring.[7] This four-membered V–O–V–O ring formed is emerging as a common motif in vanadium(V) alkoxide compounds.[4–7] In **1**, the distance from the alkoxide oxygen O2a to the other vanadium atom V1 is 3.92 Å. This distance is too large to allow the bridging motif and results in a compound without a V–O–V–O ring. Although it is possible that **1** is merely the form of the compound that crystallizes under the conditions employed in this work, the discovery of **1** lends support to proposed alternative bridging structural arrangements between vanadium(V) and 1,2-diols.

Dissolution of the colorless crystalline material **1** in chlorinated solvents is slow and results in a clear orange solution. The compound is not very soluble but, when dissolved, may in part convert to an alternative compound that is more soluble and orange in color. Variable-temperature ^{1}H and ^{51}V NMR spectra reveal that the compound undergoes complex changes in solution. The ^{51}V NMR spectrum shows the presence of two compounds at ambient temperature and suggests that the two signals at −387 and −455 ppm correspond to species with the same number of vanadium atoms. The two species observed at 25 °C are converted into three species at −50 °C: two minor resonances and one major resonance at −298 (<2%), −328 (<25%), and −482 (>70%) ppm, respectively. We presume that exchange and conformational processes are occurring and that these processes are responsible for the observed chemical shift and line width changes in the ^{51}V NMR spectrum. Since the original two resonances at −387 and −455 ppm are observed at ambient temperature in the same ratio before and after the VT studies, these processes are all reversible. The minor −298 ppm resonance will be discussed in detail in a full paper. The signal at −328 ppm is reminiscent of that found for the pinacol vanadate dimer at −324 ppm and is likely due to a dimer containing pentacoordinate vanadium in a similar bridging alkoxide structure. A complex with a similar chemical shift (−326 ppm) at ambient temperature forms between $VOCl_3$ and another vicinal diol, *cis*-1,2-cyclohexanediol. The major resonance at −482 ppm is presumably due to the dinuclear ten-membered ring observed in the solid state. This expectation is supported by the solid-state ^{51}V NMR spectrum of compound **1** giving a resonance at −474 ppm.[13] A chemical shift of −477 ppm is found when $VOCl_3$ reacts with *trans*-1,2-cyclohexanediol.[16] The restricted geometry of this ligand dictates the conformations possible in the complex, and accordingly the *trans*-1,2-cyclohexanediol would form a bridging complex with pentacoordinate vanadium(V) only at the expense of significant angle strain. The ethylene glycol ligand in **1** is not subjected to such steric limitations and accordingly forms both complexes. The reasons for the preferences of **1** await further structural and spectroscopic studies.

In general, the change from tetracoordination to higher coordination compounds is accompanied by a red shift of the first (low energy) absorption band.[9] Compounds $VO(OSiPh_3)_3$[2] and **1** contain tetrahedral vanadium centers and are colorless crystalline materials as long as water is excluded during synthesis and storage. A number of other vanadate triesters $VO(OR)_3$ containing bulky alkoxide ligands (e.g. R = $C(CH_3)_3$, $C(C_6H_5)_3$, or 1-adamantyl)[17] are also colorless and presumably four-coordinate. These compounds remain colorless in solution and have constant ^{51}V NMR chemical shifts[5,17d,18,19] at different concentrations. In triesters with small alkoxide ligands (e.g. R = CH_3, CH_2CH_3, or CH_2CH_2Cl) the coordination sphere of the vanadium is expanded by the formation of bridging dimeric or oligomeric derivatives.[4–6,17] These compounds are yellow, orange, or red and have ^{51}V NMR chemical shifts that change with increasing concentration in solution. The monochloro-substituted pinacol vanadate dimer also contains bridging alkoxide moieties and is deep red. The coordination number of oxovanadium(V) alkoxides ($VO(OR)_3$) or oxovanadium(V) chloride alkoxides ($VOCl(OR)_2$), including the vicinal diols we have prepared, correlates well with the color of these compounds, either in the solid state or in solution.

In summary, the complex formed between ethylene glycol and $VOCl_3$ $[VOCl(OCH_2CH_2O)]_2$ (**1**) has resulted in the first tetrahedrally coordinated vanadium(V) alkoxide derivative to be structurally characterized. The compound is dinuclear and consequently presents a new type of 1,2-diol bridging across two vanadium(V) atoms in oxovanadium(V) alkoxide systems.

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Supplementary Material Available: Complete tables of experimental crystallographic details, atomic coordinates, anisotropic thermal parameters of all non-hydrogen atoms, and bond lengths and angles for $[VOCl(OCH_2CH_2O)]_2$ (**1**) (4 pages). Ordering information is given on any current masthead page.

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(10) IR (KBr): 1437 (m), 1366 (s), 1341 (s), 1261 (m), 1227 (s), 1067 (vs), 1015 (vs), 923 (vs), 656 (vs), 450 (vs) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.98 (2 H, d), 5.55 (s), 5.33 (2 H, d).

(11) Empirical formula: $C_2H_4ClO_3V$. $M_r = 162.4$; triclinic, $P\bar{1}$; $a = 6.061$ (2) Å, $b = 7.068$ (2) Å, $c = 7.342$ (2) Å, $\alpha = 103.86$ (3)°, $\beta = 109.57$ (3)°, $\gamma = 104.61$ (3)°, $V = 268.05$ (14) Å^3, $Z = 2$, $D_x = 2.01$ g cm^{-3}; λ(Mo Kα) = 0.7107 Å, $\mu = 22.39$ cm^{-1}, $F(000) = 160$, $T = -100$ °C; $R = 0.032$ ($R_w = 0.076$) for 1190 unique, observed reflections. Crystal size 0.50 × 0.50 × 0.42 mm (clear, colorless cubes). Siemens R3m/V diffractometer, unit cell constants from least-squares fit of setting angles for 25 reflections ($2\theta_{av} = 21.4°$). Data collected ($\theta/2\theta$ scans) to (sin $\theta)/\lambda = 0.6497$ Å^{-1}; $-7 \le h \le 7$, $-9 \le k \le 8$, $0 \le l \le 9$. Three standard reflections (200, 030, 002) every 97; Lorentz and polarization corrections; semiempirical absorption correction applied ($T_{max} = 0.98$, $T_{min} = 0.58$, R_{merge}(bef) = 0.05, R_{merge}(aft) = 0.03); 1202 unique reflections, 1190 reflections with $F_o > 2.5\sigma(F_o)$ observed. Structure solved by direct methods (SOLV) (full-matrix least-squares, 65 parameters total, data/parameters = 18.3) weighted [$w = (\sigma^2(F) + gF^2)^{-1}$, $g = 1.2 \times 10^{-3}$] least-squares refinement on F. H atoms in idealized positions (C–H = 0.96 Å, $U(H) = 1.2U_{iso}(C)$). Non-H atoms refined with anisotropic thermal parameters. At convergence ($(\Delta/\sigma)_{max} = 0.04$, $(\Delta/\sigma)_{mean} = 0.009$ for last cycle) $R = 0.032$, $R_w = 0.076$, $S = 2.07$, $(\Delta\rho)_{max} = 0.54$ e Å^{-3}, and $(\Delta\rho)_{min} = -0.61$ e Å^{-1}. Neutral atom scattering factors and anomalous dispersion corrections used (*International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV); all calculations performed using the SHELXTL PLUS (UNIX) program library (Sheldrick, G. M. *SHELTXTL PLUS* (*UNIX*), Rev. 5; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990).

(12) Crans, D. C.; Marshman, R. W.; Gottlieb, M. S.; Anderson, O. P.; Miller, M. M. *Inorg. Chem.* **1992**, *31*, 4939.

(13) Crans, D. C.; Felty, R. A.; Eckert, H.; Das, N. Manuscript in preparation.

(14) (a) Alber, T.; Gilbert, W. A.; Ponzi, D. R.; Petsko, G. A. *Ciba Found. Symp.* **1983**, *93*, 4. (b) Wlodawer, A.; Miller, M.; Sjölin, L. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3628.

(15) Gresser, M. J.; Tracey, A. S. *J. Am. Chem. Soc.* **1986**, *108*, 1935.

(16) Viet, M. T. P.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 3026.

(17) (a) Mittal, R. K.; Mehrotra, R. C. *Z. Anorg. Allg. Chem.* **1964**, *327*, 311. (b) Witke, K.; Lachowicz, A.; Bruser, W.; Zeigan, D. *Z. Anorg. Allg. Chem.* **1980**, *465*, 193. (c) Hillerns, F.; Rehder, D. *Chem. Ber.* **1991**, *124*, 2249. (d) Crans, D. C.; Chen, H.; Felty, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 4543.

(18) Paulsen, K.; Rehder, D.; Thoennes, D. *Z. Naturforsch., A* **1978**, *33A*, 834.

(19) Lachowicz, A.; Höbold, W.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1975**, *418*, 65.