Inorg. Chem. **1996,** *35,* 6485−6494

Four- and Five-Coordinate Oxovanadium(V) Alkoxides: Do Steric Effects or Electronic Properties Dictate the Geometry?

Jean Yves Kempf,[†,‡] Bernard Maigret,*[,†] and Debbie C. Crans*[,§]

Laboratoire de Chimie Theorique, University Nancy I, B.P. 239, 54506 Vandoeuvre-les-Nancy, France, and Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872

Received February 15, 1996[⊗]

Sterically hindered ligands generally form metal complexes with lower coordination numbers than less hindered ligands. In contrast to dogma, the solid state vanadium(V) complexes with ethylene glycol and pinacol contain four- and five-coordinate vanadium atoms, respectively. *Ab initio* and electrostatic potential distribution calculations were conducted on both experimental and optimized geometries of the four- and five-coordinate oxovanadium chloroalkoxides. *Ab initio* energy calculations favor the five-coordinate species for all ligands at all levels of theory examined. No significant differences in the electrostatic properties of the vanadium atoms in the two types of molecules were observed by using electrostatic potential distribution analysis. Methyl group substitutions on the ligand did not change the electronics of the vanadium atoms sufficiently to be a factor. Thus, we conclude that neither electronics nor sterics at the metal center explains the experimental geometries. In the absence of a significant observable electronic effect at the vanadium, we note that the experimental observations can be attributed to ligand geometric effects such as the Thorpe−Ingold and/or *gem*-dialkyl effects.

Introduction

A five-coordinate trigonal bipyramidal vanadium derivative structurally resembles the transition state for hydrolysis of an organic phosphate, and vanadate derivatives have been recognized as transition state analogs for several decades.[1] The insulin mimetic properties of vanadate and other vanadium compounds currently under examination as oral insulin substitutes[2,3] have been attributed to the ability of vanadate to form such a transition state analog within tyrosine protein phosphatases.[4] Vanadate and organic vanadates have also been shown to mimic phosphate and organic phosphate analogs and accordingly are recognized as ground state analogs.[5−7] Characterization of organic vanadates with respect to structure and properties thus is important to understand when an organic vanadate will act as a transition state analog and when it will act as a ground state analog.

Organic vanadates, often referred to as oxovanadium alkoxides, have been known for almost 100 years, although structural information has only recently been available (reviewed in refs 8 and 9). The first structural information provided little similarity with the corresponding phosphate derivative since vanadium in $VO(OCH_3)_3$ is in an octahedral environment.[10] More recent examples such as $VO(OCH_2CH_2Cl)_3$[11] and $VO(OC_5H_9)_3$[12] demonstrate that some oxovanadium alkoxides contain five-coordinate vanadium. Furthermore, a silyl derivative $[VO(OSi(C_6H_5)_3)_3]$ shows that vanadium can exist in a four-coordinate environment.[13] Although several tetrahedral oxovanadium alkoxides have been prepared in solution, none of these have been characterized by X-ray crystallography.[14] The current interest in the mechanism and applications of the oxidation of organic compounds by vanadium oxides would benefit from detailed understanding of the subtle factors that affect the coordination chemistry of simple oxovanadium alkoxides.[15]

The first report of an organic vanadate derivative acting as a transition state analog was the vanadate−uridine complex interacting with the enzyme ribonuclease.[1] Studies have been carried out to characterize the many vanadium species in solution (reviewed in ref 9), but until recently no solid state structural information was available for the major species due to experimental difficulties (disorder, twinning, etc.).[16] Thus, two model systems have been developed: one in which one O^- group is replaced by a chlorine atom[17,18] and another in which the diol ligand was replaced by an α-hydroxy acid.[19] In both of these

---

[†] University Nancy I.

[‡] Current address: Rhone-Poulenc, Centre de Recherches d'Aubervilliers, Computational Chemistry, 52 rue de La Haie Coq, F-93308 Aubervilliers Cedex, France.

[§] Colorado State University.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Lindquist, R. N.; Lynn, J. L., Jr.; Lienhard, G. E. *J. Am. Chem. Soc.* **1973**, *95,* 8762−8768.

(2) Posner, B. I.; Faure, R.; Burgess, J. W.; Bevan, A. P.; Lachance, D.; Zhang-Sun, G.; Fantus, I. G.; Ng, J. B.; Hall, D. A.; Soo Lum, B.; Shaver, A. *J. Biol. Chem.* **1994**, *269,* 4596−4604.

(3) McNeill, J. H.; Yuen, V. G.; Hoveyda, H. R.; Orvig, C. *J. Med. Chem.* **1992**, *35,* 1489−1491.

(4) Stankiewicz, P. J.; Tracey, A. S.; Crans, D. C. *Metal Ions in Biological Systems;* Sigel, H., Sigel, A., Eds.; Marcel Dekker, Inc.: New York, 1995; pp 287−324.

(5) Nour-Eldeen, A. F.; Craig, M. M.; Gresser, M. J. *J. Biol. Chem.* **1985**, *260,* 6836−6842.

(6) Drueckhammer, D. G.; Durrwachter, J. R.; Pederson, R. L.; Crans, D. C.; Daniels, L.; Wong, C.-H. *J. Org. Chem.* **1989**, *54,* 70−77.

(7) Crans, D. C.; Simone, C. M.; Blanchard, J. S. *J. Am. Chem. Soc.* **1992**, *114,* 4926−4928.

(8) Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30,* 148−167.

(9) Crans, D. C. *Metal Ions in Biological Systems;* Sigel, H., Sigel, A., Eds.; Marcel Dekker, Inc.: New York, 1995; pp 147−209.

(10) Caughlan, C. N.; Smith, H. M.; Watenpaugh, K. *Inorg. Chem.* **1966**, *5,* 2131−2134.

(11) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1990**, *29,* 3013−3019.

(12) Hillerns, F.; Olbrich, F.; Behrens, U.; Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31,* 447−448.

(13) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1991**, *30,* 1689−1694.

(14) Crans, D. C.; Chen, H.; Felty, R. A. *J. Am. Chem. Soc.* **1992**, *114,* 4543−4550.

(15) Cristiani, C.; Forzatti, P.; Busca, G. *J. Catal.* **1989**, *116,* 586−589.

(16) Angus-Dunne, S. J.; Batchelor, R. J.; Tracey, A. S.; Einstein, F. W. B. *J. Am. Chem. Soc.* **1995**, *117,* 5292−5296.

(17) Crans, D. C.; Felty, R. A.; Miller, M. M. *J. Am. Chem. Soc.* **1991**, *113,* 265−269.

(18) Crans, D. C.; Felty, R. A.; Anderson, O. P.; Miller, M. M. *Inorg. Chem.* **1993**, *32,* 247−248.

(19) Hambley, T. W.; Judd, R. J.; Lay, P. A. *Inorg. Chem.* **1992**, *31,* 343−345.

S0020-1669(96)00170-X CCC: $12.00

cases, crystal and solution structures were obtained for each cyclic vanadium derivative. In general, the coordination geometry about the metal atom in compounds is the result of electronic and/or geometric effects. However, oxovanadium chloroalkoxides have geometries around the vanadium atoms that follow a counterintuitive pattern: *the more bulky ligand generates the five-coordinate compound, and the less bulky ligand forms the four-coordinate vanadium compound.*

In this study, we examine the structure, electronic properties, and stability of three four- and five-coordinate cyclic oxovanadium chloroalkoxides to determine the factors influencing the coordination number around the vanadium. Since only minor changes were observed in the electronic properties of the respective vanadium atoms, and steric effects around the metal would predict the opposite stability pattern, alternative effects such as steric factors on the ligand should be considered. In summary, our experimental and theoretical observations are consistent with the Thorpe−Ingold[20] effect and/or the *gem*-dialkyl effect[20] and suggest that the differences in coordination number around the vanadium atom are attributed to the subtle geometric effects induced in the ligand.

Experimental Section

Programs and Facilities. An all-electron Hartree−Fock SCF calculation was carried out on the 3090 IBM computer of the CIRCE (Orsay, France), using the Gaussian 88 program for preliminary investigations.[21] In the later studies including the optimizations and in the determinations of the topological properties of the molecules, the Cray YMP16-C90 (Eagan) with the Gaussian 92[22] programs were used.

Basis Sets. Molecules containing third-row atoms are described well by 14s-type, 9p-type, and 5d-type functions.[23] These are large basis sets that yield a value of the total energy close to the Hartree−Fock limit and that for larger molecules require extraordinarily large amounts of computer time. When calculations on transition metal complexes with a relatively large number of ligand atoms are under investigation, the calculation can be approximated by a medium basis set for third-row atoms.[24] The basis set used here for vanadium contains 12s, 6p, and 4d functions optimized for the lowest state of the $3d^n4s^2$ neutral atom configuration. Six, two, two, and two 1s functions are used for the 1s, 2s, 3s, and 4s atomic orbitals, respectively, four and two 2p functions are used for the 2p and 3p atomic orbitals, respectively, and four 3d functions for the 3d atomic orbitals. Addition of a d-type orbital with an exponent of 0.0885 on the vanadium atoms in this basis set significantly improves the representation of the vanadium atom.[25] Not only is the augmented 12s, 6p, and 4d set more economical in integral evaluation but it also performs nearly as well as the augmented 12s, 6p, and 5d set in molecular applications. The last 4p atomic orbitals were created by adding a p orbital with an exponent of 0.22. Thus, the basis set for vanadium adopted in the present study is expressed as (12s7p5d)/[5s3p2d]. The exponents and contraction coefficients for the vanadium atom are detailed in the supporting information.

Reliable qualitative information for molecules can be obtained from less accurate wave functions for first-row atoms. These wave functions were built from medium-size basis sets ranging from 7s,3p to 9s,5p.[26−29] The exponent and contraction coefficients for carbon, oxygen, chlorine, and hydrogen are also detailed in the supporting information. The current calculation gives geometries in excellent agreement with the experiment. Due to the fact that the presence of polarization functions increases the V−O and V−Cl distances by 0.2 Å, thus generating structures in poor agreement with experiments, and given our focus on structure and electrostatic description, we chose not to include polarization functions in our optimization and calculations described here. (Furthermore, exhaustive use of polarization functions in these calculations is unrealistic because of the significant expense in calculating these large systems.)

Point Charge Calculations. Charges were computed from a Mulliken analysis[30] and from self-consistent field molecular electrostatic properties (SCFMEP) by fitting the molecular electrostatic potential. In this last procedure, suitable point charges were placed at the atomic centers of the molecule to reproduce the SCFMEP using a least-squares calculation.[31] The fitting procedure has been constrained so that the sum of the atomic charges is equal to the total molecular charge. The sampling algorithm used is equivalent to the one adopted by Cox and Williams.[32]

Electrostatic Potentials. Electrostatic potentials have been computed for planar grids of points defined in the plane containing the four oxygen and two vanadium atoms. The spherical investigations for the electrostatic potential are centered on oxygen and chlorine sites and are represented in two dimensions by means of a stereographic projection.[33] Although the choice of basis set may alter the calculation of electronic properties, such as the electrostatic potential, this representation [(12s7p5d)/(5s3p2d)] gives results similar to an improved representation in calculations of $V_{10}O_{28}{}^{6-}$.[34]

Experimental Geometry for Fixed-Point Calculations. The geometry used for the self-consistent field (SCF) calculation of the oxovanadium(V) ethane-1,2-diolate chloride ($V_2O_6Cl_2C_4H_8$) (**1**) was created from the experimental structure for di(*μ*-pinacolato)bis[oxovanadium(V) chloride] (**2**), ($V_2Cl_2O_6C_{12}H_{24}$).[17] Structure **1** was obtained by removing the four methyl groups from the pinacolate ligand, replacing them with hydrogens atoms using the Sybyl program package,[35] and adjusting the bond lengths appropriately. The geometry for the monomer, **4**, was created by removing the fraction of the molecule that was related to the monomeric unit by the center of inversion.

Optimized Geometry. The space group for compounds **1**−**3** is $P\bar{1}$, defining 11 inequivalent atoms in a molecule with an inversion center. When no symmetry restraints are invoked, a full geometry optimization of compounds **1** and **3** involves the variation of 60 parameters. These parameters include 21 bond lengths, 20 internuclear angles, and 19 internuclear dihedral angles. The monomer structure, **4**, was optimized in an analogous manner by using Berny's algorithms as implemented in the Gaussian packages.[21,22]

Results and Discussion

Point (12s7p5d)/[5s3p2d] Calculation on Structure 1. The geometry determined by X-ray crystallography for di(*μ*-pina-

---

(20) Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224−232.

(21) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. *Gaussian 88*; Gaussian, Inc: Pittsburgh, PA, 1988.

(22) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*; Gaussian, Inc: Pittsburgh, PA, 1992.

(23) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52,* 1033−1036.

(24) (a) Roos, B.; Veillard, A.; Vinot, G. *Theor. Chim. Acta (Berlin)* **1971**, *20,* 1−11. (b) Hay, P. J. *J. Chem. Phys.* **1977**, *66,* 4377−4384. (c) At the request of a reviewer, we repeated the geometry optimization with the corresponding basis set including diffuse functions on the chlorine and oxygen atoms. This modification of the basis set did not affect our results and conclusions. This is evident from the following observations: (1) The exponent for the diffuse sp functions for the chlorine and oxygen atoms are 0.0483 and 0.0845, respectively. (2) There are no significant changes in the geometries. (3) The newly obtained energy is lower than the previous one by 0.2995 kcal/mol for **1**, 3.3027 kcal/mol for **3**, and 0.4277 kcal/mol for **4**.

(25) Ribeiro-Claro, P. J. A; Amado, A. M.; Teixeira-Dias, J. J. C. *J. Comput. Chem.* **1996**, *17,* 1183−96.

(26) Clementi, E. *J. Chem. Phys.* **1967**, *46,* 4737−4742.

(27) Whitman, D. R.; Hornback, C. J. *J. Chem. Phys.* **1969**, *51,* 398−402.

(28) Roos, B.; Siegbahn, P. *Theor. Chim. Acta (Berlin)* **1970**, *17,* 199−209.

(29) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102,* 939−947.

(30) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23,* 1833−1840.

(31) Chipot, C.; Maigret, B.; Rivail, J.-L.; Scheraga, H. A. *J. Phys. Chem.* **1992**, *96,* 10276−10284.

(32) Cox, S. R.; Williams, D. E. *J. Comput. Chem.* **1981**, *2,* 304−323.

(33) Stevens, E. D.; Coppens, P. *J. Cryst. Mol. Struct.* **1978**, *7,* 251−255.

(34) Kempf, J.-Y.; Rohmier, M.-M.; Poblet, J.-M.; Bo, C.; Bénard, M. *J. Am. Chem. Soc.* **1992**, *114,* 1136−1146.

(35) *Theory Manual*; TRIPOS Associates Inc.: 1699 S. Hanley Rd., Saint-Louis, MO 61344-2913, 1994.

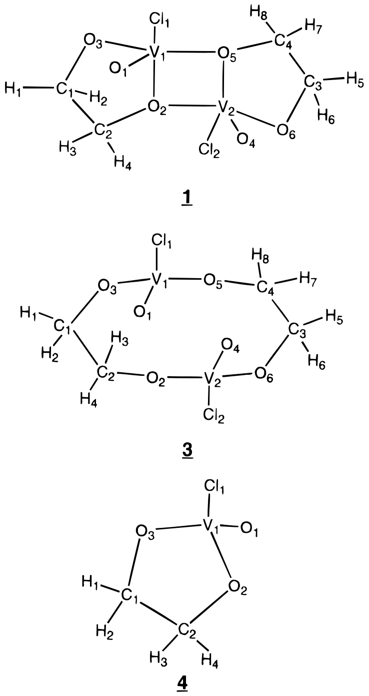

Figure 1. The numbering systems used in compounds **1**, **3**, and **4**.

Table 1. Selected Structural Parameters for Compounds **1**−**4**

bond length	compd **1** opt	compd **2**[a] exp	compd **3**[b] exp	compd **3**[b] opt	compd **4** opt
V_1-Cl_1	2.261	2.219(1)	2.207(1)	2.238	2.232
V_1-O_1	1.554	1.576(1)	1.578(2)	1.556	1.561
V_1-O_2	1.944	1.967(1)		(3.72)	1.758
V_1-O_3	1.765	1.773(1)	1.741(2)	1.735	1.757
V_1-O_5	1.928	1.964(1)	1.743(2)	1.735	
O_2-C_2	1.464	1.466(2)	1.433(3)	1.444	1.469
O_3-C_1	1.448	1.451(2)	1.422(2)	1.444	1.463
C_1-C_2	1.532	1.557(3)	1.505(3)	1.514	1.546

bond angle	compd **1** opt	compd **2**[a] exp	compd **3**[b] exp	compd **3**[b] opt	compd **4** opt
$O_1-V_1-O_2$	113.4	117.6(1)			117.6
$O_1-V_1-O_3$	105.8	101.4(1)	107.1(1)	107.5	101.4
$O_1-V_1-Cl_1$	108.8	106.7(1)	108.3(1)	107.4	106.7
$O_2-V_1-O_3$	79.3	79.7(1)			79.7
$O_2-V_1-O_5$	71.0	71.4(1)			
$O_2-V_1-Cl_1$	136.2	135.0(1)			99.3
$O_3-V_1-O_5$	146.0	149.3(1)	110.2(1)	114.1	
$C_1-O_3-V_1$	122.5	119.1(1)	134.0(2)	136.3	119.1
$C_2-O_2-V_1$	117.7	116.3(1)	135.3(2)	136.3	116.3
$C_2-C_1-O_3$	104.1	102.2(1)	109.8(2)	108.2	104.6
$C_1-C_2-O_2$	102.3	102.1(1)	109.5(2)	108.2	104.5

[a] Reported in ref 17. [b] Reported in ref 18.

colato)bis[oxovanadium(V) chloride] (**2**) ($V_2Cl_2O_6C_{12}H_{24}$) was modified to that of **1**, and then a point calculation was carried out. Structure **2** was modified to structure **1** because the additional eight methyl groups would render the compound too large for an unconstrained geometry optimization.

Geometry Optimization. The two binuclear molecules contain inversion centers; however, no restraints were imposed and 60 parameters were varied in the geometry optimization. The connectivities of the atoms in compounds **1**, **3**, and **4** are shown in Figure 1, and selected structural parameters are listed in Table 1. One vanadium atom, V_1, is coordinated to one chlorine atom and four oxygen atoms, O_1, O_2, O_3, and O_5, where O_5 is related to O_2 by an inversion center. The optimized bond lengths between the vanadium atom and the oxygen atoms are in excellent agreement with the experimental structure. They are all consistently underestimated by less than 2%. In contrast, the bond length between the vanadium atom and the chlorine atom was overestimated by 2% in the optimized structure. The interatomic angles in the experimentally derived and optimized structures were also in agreement, with a less than 5% difference observed for any angle. The minimum difference was observed for $\angle O_1V_1O_5$ with a magnitude of 0.2%, and the maximum difference was observed for $\angle O_1V_1O_3$ with a magnitude of 4.4%. In Figure 2a the optimized geometry of **1** is overlaid on the experimentally determined structure, showing little change in the environment about the vanadium atom between the experimental and optimized geometries.

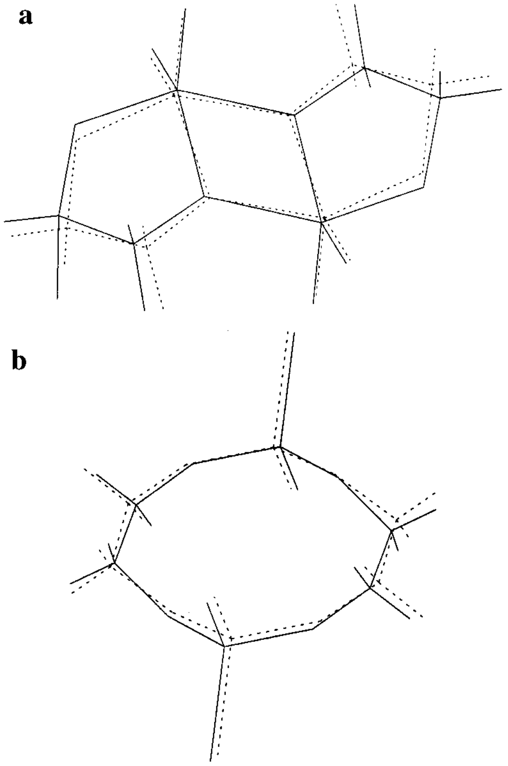

Figure 2. Experimental structures compared to the optimized geometries: (a) compound **1** and (b) compound **3**. The experimental geometry is shown in solid lines and the optimized geometry in broken lines.

Optimization of the experimental structure of compound **3** also yielded a structure very similar to the dimeric structure characterized by X-ray crystallography for compound **3** (Figure 2b). In this molecule, one vanadium atom, V_1, is coordinated to one chlorine atom and three oxygen atoms, O_1, O_2, and O_3, in a tetrahedral geometry. The bond lengths in this compound are again within 2%, with the V−O bonds being underestimated and the V-Cl bond length being overestimated. In the interatomic bond angles the differences are less than 4% between the experimental and optimized structures. The smallest difference of 0.2% was found for $\angle Cl_1V_1O_5$, and the largest difference of 3.6% was found for $\angle O_3V_1O_5$. We conclude that this level of theory is able to provide meaningful geometries for these types of vanadium compounds. These findings lend support to further studies using this basis set in calculating the geometries of similar vanadium compounds that are not structurally characterized.

The geometry optimization of compound **4** (the monomeric unit of compound **1**) involves the optimization of a compound containing a tetrahedral vanadium bound to one chlorine atom and three oxygen atoms, O_1, O_2, and O_3. The V_1-O_1 bond was found to be 1.561 Å, whereas the V_1-O_2 and V_1-O_3 bonds were 1.757 and 1.758 Å, respectively. So although the initial structure provided was highly asymmetric, the optimization generated a near-symmetrical structure with V−O bond lengths

Table 2. Isodesmic Reactions; Dimerization and Ring Contraction

	$U(\mathbf{4})$	$U(\mathbf{1})$	ΔU (hartree)	ΔU (kcal/mol)
	Experimental Geometries			
SCF	−1699.24711426	−3398.70485571	−0.2106	−132.9
Boys/Bernardi	−1699.27454322	−3398.70485571	−0.1558	−97.7
	Optimized Geometries			
SCF	−1699.28475212	−3398.71653739	−0.1470	−92.3
Boys/Bernardi	−1699.28972055	−3398.71653739	−0.1371	−86.0
MP2 Møller−Plesset	−1700.16677928	−3400.45978508	−0.1262	−79.2

	$U(\mathbf{3})$	$U(\mathbf{1})$	ΔU (hartree)	ΔU (kcal/mol)
	Experimental Geometries			
SCF	−3398.56339899	−3398.70485571	−0.1415	−88.8
	Optimized Geometries			
SCF	−3398.67340071	−3398.71653739	−0.0431	−27.0
MP2 Møller−Plesset	−3400.43162235	−3400.45978508	−0.0282	−17.7

similar to those found in compounds **1** and **3**. Furthermore, once the two units in the dimeric **1** are separated, the angles surrounding the five-coordinate vanadium atom are optimized to a tetrahedral vanadium atom (from the five-coordinate vanadium atom in the dimer). Accordingly, compound **4** shows its preferred geometry analogous to that found for trialkyl phosphate esters of vicinal diols,[36,37] thus supporting the phosphorus−vanadium analogy.

Isodesmic Reactions. The dimerization energy required to transform compound **4** into compound **1** (eq 1) can be calculated from eq 1 as shown in eq 2. Table 2 lists the energies for reaction 1 obtained by using the experimental geometry, the optimized geometry, and the approach used by Boys and Bernardi in which ghost orbitals are used to overcome the problem of overestimation of ΔU.[38] As seen from Table 2, the dimerization energy estimates ranged from −80 to −133 kcal/mol. This result supports the fact that no evidence has been obtained for the monomeric unit in the solid state or in solution, although improving the basis set will generate a better quantitative description of this reaction.

$$\mathbf{4} + \mathbf{4} \rightarrow \mathbf{1} \tag{1}$$

$$\Delta U = U(\mathbf{1}) - 2U(\mathbf{4}) \tag{2}$$

Dissolution of compound **3** generates a mixture of dimeric four- and five-coordinate compounds. The isodesmic reaction shown in eq 3 has a ΔU defined as shown in eq 4. The energies obtained from experimental and optimized geometries are shown in Table 2, and they show that this reaction is more favorable than reaction 1. The energy difference between **1** and **3** is calculated to be −18 kcal/mol, with compound **1** as the favored species. Improving the basis set should provide an energy gap closer to that observed experimentally, as indicated in the point calculation using the approach by Boys and Bernardi and a point calculation using the MP2 Møller−Plesset second-order approximation calculation (Table 2). The 18 kcal/mol is, however, somewhat higher than the energy difference observed in nonpolar solution;[18] both compounds are observed in a ratio of 1:3, favoring compound **1**. We conclude that compounds **3** and **1** are significantly closer in energy than **1** and two molecules of compound **4**.

$$\mathbf{3} \rightarrow \mathbf{1} \tag{3}$$

$$\Delta U = U(\mathbf{1}) - U(\mathbf{3}) \tag{4}$$

Comparison of the properties of compounds **1**, **3**, and **4**, which represent vanadium compounds in both four- and five-coordinate geometries, will allow us to obtain more insight into the nature of these compounds and the stability of compound **1**. Therefore, we will examine and compare the dipole moments, orbitals, and electrostatic potentials in all three compounds.

Dipole Moments. Centrosymmetric forms of compounds **1** and **3** have dipole moments equal to zero. The dipole moment for compound **4** is 4.800 D, documenting the polar nature of this compound. Dissolution of compound **3** in nonpolar organic solvents such as CH_2Cl_2, $CHCl_3$, and benzene generates compound **1**, whereas no evidence for compound **4** was observed by ^{51}V NMR spectroscopy, in accord with the expected limited solubility of a polar compound in a nonpolar solvent.[18]

Molecular Orbitals, Electron Affinity, Ionization Potential, and Hardness. A population analysis based on the SCF density calculation provides the molecular orbitals and their corresponding energies. For all three compounds, several molecular orbitals around the HOMO−LUMO gap are nonbonding orbitals. In addition, most orbitals for compounds **1** and **3** are mixed with others of similar symmetry, and the mixing is so extensive that it is difficult to localize many of the orbitals. Localization of the orbitals using the natural bonding orbitals (NBO)[39] was of only limited use in the examination of these compounds since the orbital mixing is key for the reactivity and geometries for these types of molecules. Furthermore, Koopman's theorem must be used carefully in these systems. However, analysis of both the mixed as well as the NB orbitals provided some insight into the observed geometries and reactivities of these molecules.

The HOMO for compound **1** has electron density mainly on the chloride atom and mostly in a nonbonding manner (slight orbital mixing with the bridging, nonterminal oxygen atom was observed). In contrast, the HOMOs of both compounds **3** and **4** vary from the HOMO of compound **1** in that these orbitals have the most electron density on the nonterminal oxygen atoms. The fact that the HOMOs for all three oxovanadium alkoxides have nonbonding orbitals on basal substituents supports the recent studies on vanadium oxide catalysts (the reactivity of these catalysts is attributed to discrete oxovanadium pseudo-tetrahedral centers).[40] In these studies, the HOMO was reassigned from a V═O orbital to a nonbonding orbital with electron density on the basal oxygen atoms. In view of the very different geometries enjoyed by these three oxovanadium alkoxides, our results support the hypothesis[40] that nonbonding orbitals with electron density on basal substituents will, in general, be the HOMO in these types of molecules.

Attempts to substitute the Cl with OR, NR_2, and other nucleophiles experimentally were found to be much more difficult than anticipated, leading to the decomposition of compounds **1** and **3**.[17,18] Examination of the molecular orbitals of compounds **1** and **3** demonstrates that the virtual V-Cl bonds are so far removed from the HOMO−LUMO gap that reaction between a nucleophile and these orbitals could be problematic. In addition, lower lying virtual V−O bonds could support reactions at the V−O bonds for both molecules, in agreement with the experimental observations.

The molecular orbitals of compound **4** also show extensive orbital mixing and a series of nonbonding orbitals around the HOMO−LUMO gap. Dimerization does, however, take place

---

(36) Dutasta, J. P.; Guimaraes, A. C.; Martin, J.; Robert, J. B. *Tetrahedron Lett.* **1975**, *18*, 1519−1522.

(37) Dutasta, J. P.; Grand, A.; Guimaraes, A. C.; Robert, J. B. *Polyhedron* **1979**, *35*, 197−207.

(38) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 533−566.

(39) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 899−926.

(40) Tran, K.; Hanning-Lee, M. A.; Biswas, A.; Stiegman, A. E.; Scott, G. W. *J. Am. Chem. Soc.* **1995**, *117*, 2618−2626.

Table 3. Total Point Charges (atomic units) for Compounds **1**, **3**, **4**, and **5** evaluated by Mulliken and SCF Molecular Electrostatic Properties SCFMEP

	compound **1**		compound **3**		compound **4**		compound **5**	
atom	SCFMEP	Mulliken	SCFMEP	Mulliken	SCFMEP	Mulliken	SCFMEP	Mulliken
V	1.115	1.416	1.136	1.346	1.699	1.340	1.156	1.406
Cl	−0.414	−0.421	−0.388	−0.400	−0.482	−0.419	−0.425	−0.427
O_1	−0.401	−0.333	−0.403	−0.385	−0.523	−0.335	−0.411	−0.339
O_2	−0.305	−0.821	−0.429	−0.692	−0.611	−0.670	−0.297	−0.824
O_3	−0.510	−0.636	−0.429	−0.692	−0.623	−0.640	−0.593	−0.639
C_1	0.041	−0.117	−0.033	−0.088	−0.209	−0.115	−0.754	−0.115
C_2	−0.002	−0.116	−0.033	−0.088	−0.132	−0.111	−0.423	−0.053
H_1	0.114	0.244	0.139	0.248	0.069	0.238	−0.628	−0.579(C)
H_2	0.133	0.255	0.151	0.252	0.089	0.245	−0.628	−0.576(C)
H_3	0.109	0.262	0.151	0.252	0.159	0.234	0.228	0.259
H_4	0.121	0.267	0.139	0.248	0.147	0.235	0.205	0.260

easily, and indeed high-lying occupied orbitals with high electron density on the oxygen atoms are identified that can readily be combined with low-lying virtual orbitals with electron density at the vanadium atom. The two lowest lying virtual orbitals, both of which have orbital energies less than 0 (see the following), attest to the high reactivity of this compound.

The electron affinity, $-\epsilon_{\mathrm{LUMO}}$,[41] for compounds **1**, **3**, and **4** is −0.0024, −0.0024, and +0.0051 hartree with this level of theory compared to −0.0022, −0.0287, and −0.0100 hartree, respectively, obtained in a Møller−Plesset second-order approximation calculation in the preceding series.

The ionization potential can be described as $-\epsilon_{\mathrm{HOMO}}$[41] and is found to be +0.4420, +0.4420, and +0.4371 hartree for compounds **1**, **3**, and **4**, respectively.[42] No experimental information is available for comparison of these ionization potentials. The absolute hardnesses were all low (0.2222, 0.2222, and 0.2160) for compounds **1**, **3**, and **4**, respectively.[43]

Atomic Point Charges. The point charges for compounds **1**, **3**, and **4** were calculated by using both the Mulliken population analysis and the net atomic charges from fits of SCF molecular electrostatic properties, as described previously.[31] The results are shown in Table 3 for compounds **1**, **3**, and **4**. The Mulliken population analysis shows that the dimer contains a vanadium atom with a higher positive charge than the monomer, which is not in agreement with the polar nature of compound **4** shown here. In view of the problems Mulliken population analysis has in reproducing electrostatic potentials in complex systems,[44] we also carried out a net atomic charge analysis using the SCFMEP[31] and the results are shown in Table 3. The SCFMEP calculation shows that the vanadium atom in compound **1** is less charged than the vanadium atom in compound **4** by 0.58 (Table 3), which is in accord with chemical expectations and experimental observations for these compounds.

Analysis of the atomic point charges further shows that only atoms that are coordinated to the vanadium atom contribute to the final charge on the vanadium atom. Thus, the bonds represented by V_1—Cl_1, V_1—O_1, V_1—O_2, V_1—O_3, and V_1—O_5 are significant contributors for compound **1** and all others are near zero, including the bond between the two vanadium atoms. For the V_1—O_1 and V_1—O_3 bonds the number of electrons on the vanadium varies from 0.6 to 0.8 electron for each bond in compound **1**. The high concentration of electrons suggests that these bonds in compound **1** are strong. This finding supports the calculation for the vanadate monoester in which the V—O_1 type (V═O) of bond was maintained upon expansion of the vanadium coordination sphere, in contrast to the P═O bond in corresponding phosphate ester.[45] The V_1—O_2 and V_1—O_5 bonds in the dimer do not follow this trend since the 0.3 electron in these bonds documents the weak bonding in the V_2O_2 unit. For compounds **3** and **4** the contribution from the V_1—O_5 bond is near zero.

The Mulliken point charges show that compound **3** has a smaller charge on the vanadium atom than compound **1**. This pattern is reversed on the basis of SCFMEP calculations, which show that compound **1** has a lower charge on the vanadium atom than compound **3** (Table 3). The population analysis did, however, show that the V_1−O_1 contained 0.8 electron and that the V_1−O_2 and V_1−O_3 bonds contained 0.6 electron each (O_2 and O_3 are identical in this molecule). Thus, compound **3** on the average contains stronger bonds than compound **1**, and given the fact that compound **1** is more stable with more highly substituted ligands, the combination of strong and weak bonds in compound **1** apparently overall is more favorable (compound **1** is here used as a model for compound **2**).

In comparing the point charges of compounds **3** and **4**, which both contain tetrahedral vanadium atoms, Mulliken analysis suggests that both vanadium atoms have the same charge, 1.34, which is lower than the 1.42 for compound **1**. However, when the SCF molecular electrostatic properties are used, one finds that vanadium atoms in compounds **3** and **4** have higher charges than the vanadium atoms in compound **1**. In the case of compound **3** this difference is insignificant (0.02), but in compound **4** the difference is significant (0.58). The difference in charge on the vanadium atom is presumably important for the reactivity of these compounds since the vanadium as the monomer is so electrophilic that none of it is observed in solution.

Electrostatic Potential Distribution. To further probe the molecular electronic structure and reactivity patterns, we have carried out electrostatic potential calculations on compound **1**. The electrostatic potential, $V(r)$ at a reference point, r, with a molecular charge distribution $p(r)$, is given by eq 5.[46] Given the delicate balance between nuclear and electronic terms in eq 5, the electrostatic potential can take positive, zero, and negative values. Each molecule possesses a rich topographic pattern that reflects the locations susceptible to nucleophilic and electrophilic attack within the molecule.

$$V(\vec{r}) = \sum_A \frac{Z_A}{|r - \vec{R}_A|} - \int p(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \, d^3\vec{r}'$$

The asymmetric vanadium atom contains three types of V−O bonds and three different types of oxygen sites. The terminal

---

(41) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734−740.

(42) In an MP2 Møller−Plesset second-order approximation calculation, the corresponding $-\epsilon_{\mathrm{HOMO}}$ is 0.4419, 0.4427, and 0.4530 hartree for compounds **1**, **3**, and **4**.

(43) The absolute hardnesses derived from an MP2 Møller−Plesset second-order approximation were 0.2221, 0.2357, and 0.2315 for compounds **1**, **3**, and **4**, respectively.

(44) Williams, D. E.; Yan, J. M. *Adv. Atom. Mol. Phys.* **1988**, *23*, 87−130.

(45) Krauss, M.; Basch, H. *J. Am. Chem. Soc.* **1992**, *114*, 3630−3634.

(46) Daudel, R.; Leroy, G.; Peeters, D.; Sana, M. *Quantum Chemistry*; Wiley Interscience: New York, 1983.

oxygen atom, O_1, at the corner of the distorted trigonal bipyramid has an environment and a covalent nature similar to those of oxygen sites in vanadium oxides. The O_2 oxygen atom, at the side corner of the trigonal bipyramid, is bound to one carbon and two vanadium atoms in the V_2O_2 unit. The point charge calculations suggest that the V−O bonds in the V_2O_2 units are fairly ionic. The O_3 oxygen atom is coordinated to one carbon atom and one vanadium atom at the top of the trigonal bipyramid.

The electrostatic potential was calculated and displayed in three different planes for compounds **1** and **3** using the notation shown in Figure 1. For compound **1**, the first plane contains the inversion point of the molecule with $z = 0.0$ Å. This plane passes through most of the atoms in the molecule, including both the O_2 and O_3 oxygen sites (Figure 3a). The second plane lies in the section $y = 0.0$ Å and represents the electrostatic potential environment near the O_1 oxygen (Figure 3b). The third plane is perpendicular to the previous ones and lies at a distance of $y = 1.5$ Å. This plane passes through the O_2 oxygen sites (Figure 3c). In Figure 3a,b successive contour intervals are separated by 0.01 hartree, beginning from the deepest minimum found in each section, −0.070 95 and −0.046 83 hartree, respectively. In Figure 3c, successive contour intervals are separated by 0.001 hartree, beginning from the deepest minimum found in this section (−0.005 29 hartree).

For compound **3**, the first plane contains the inversion point of the molecule with $z = 0.0$ Å. This plane passes through most of the atoms in the molecule, including both the O_3 and O_6 oxygen sites (Figure 4a). The second plane lies in the section $y = 0.0$ Å and represents the electrostatic potential environment near the O_1 oxygen (Figure 4b). The third plane is parallel to the previous plane but lies at a distance of $y = 1.5$ Å. This plane passes through the O_5 and O_6 oxygen sites (Figure 4c). In Figure 4a,b, successive contour intervals are separated by 0.01 hartree, beginning from the deepest minima found in each section (−0.039 98 and −0.048 30 hartree). In Figure 4c, successive contour intervals are separated by 0.005 hartree, beginning from the deepest minimum found in this section (−0.053 45 hartree). The dashed contours represent the negative values of the electrostatic potential distribution.

The minimum at the O_3 site (−0.070 95 hartree) is connected by a narrow gorge through a high saddle point (−0.032 90 hartree) to another minimum at −0.044 62 hartree associated with the chlorine atom. This valley is visible in Figure 3a for both sides of compound **1**. In Figure 3b a third minimum with an energy of −0.046 83 hartree connected to O_1 is observed. No potential well was found associated with O_2. In Figure 4a the deepest minimum in this section (−0.039 98 hartree) is connected to the chlorine atom. In Figure 4b,c other minima are associated with O_1 (−0.048 31 hartree), O_2 (or O_5, −0.053 45 hartree) and O_3 (or O_6, −0.053 45 hartree) oxygen sites. The facts that no minimum is associated with the O_2 oxygen atom in compound **1** and that one minimum has been found in compound **3** may reflect that the O_2 oxygen site is sp hybridized in **3** and becomes sp^2 hybridized in compound **1**. The fact the oxygen atoms having fewer bonds have deeper minima in these compounds is opposite what is observed for the decavanadate anion in which the sp^3-hybridized oxygen atoms were more basic than the sp-hybridized oxygen atoms.[34] The possibility that this observation is an artifact of the basis set is not likely, since improved calculations of a related system showed no change in the location of minima.[34] Perhaps these differences can be traced to whether the oxygens are alkoxide oxygen atoms or simply oxide oxygen atoms.

The preceding studies are not sufficient to identify the global minimum, since such a minimum could lie in a horizontal plane

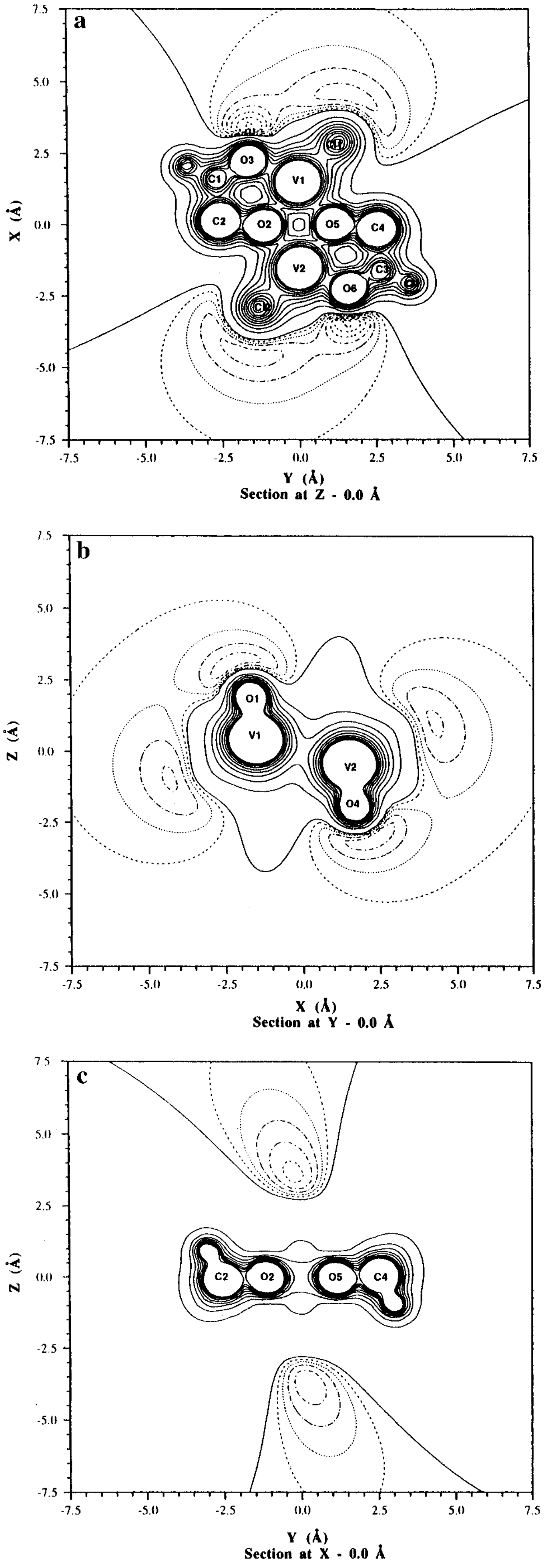

Figure 3. Electrostatic potential distribution map for compound **1** in three different planes: (a) $z = 0.0$ Å containing the inversion point of the molecule; (b) $y = 0.0$ Å; and (c) $x = 0.0$ Å. The numbering system shown in Figure 1 is employed.

containing the appropriate oxygen and chlorine atoms. However, we can conclude that the observed minima are connected to a specific oxygen site located at a distance between 1.10 and 1.40 Å, whereas the observed minimum connected to the chlorine is located at a distance between 1.40 and 2.0 Å. This information suggests that minima could easily be identified by using spherical cross sections centered on a given oxygen or chlorine atom. For compound **1**, the respective energies for minima associated with the oxygen atoms are 0.081 98 hartree for O_3 at a distance of 1.173 Å and −0.047 14 hartree for O_1 at a distance of 1.306 Å. Again, no potential wells were found in the vicinity of the O_2 oxygen sites. An energy minimum of −0.046 02 hartree has been found around the chlorine atom at a distance of 1.798 Å. For compound **3** the respective minimum energies for the oxygen atoms are −0.054 30 hartree for O_3 at a distance of 1.169 Å, −0.054 25 hartree for O_2 at a distance of 1.169 Å, and −0.048 13 hartree for O_1 at a distance of 1.274 Å. An energy minimum of −0.042 50 hartree has been found around the chlorine atom at a distance of 1.803 Å. In both compounds the lowest minimum is connected to the O_3 oxygen site, and this minimum is more stable by 21.9 kcal/mol than the one associated with O_1 in compound **1**. In compound **3** the oxygen sites O_2 (or O_5) and O_3 (or O_6) have similar minimum energies and are more stable than the one associated with the O_1 site by 3.9 kcal/mol.

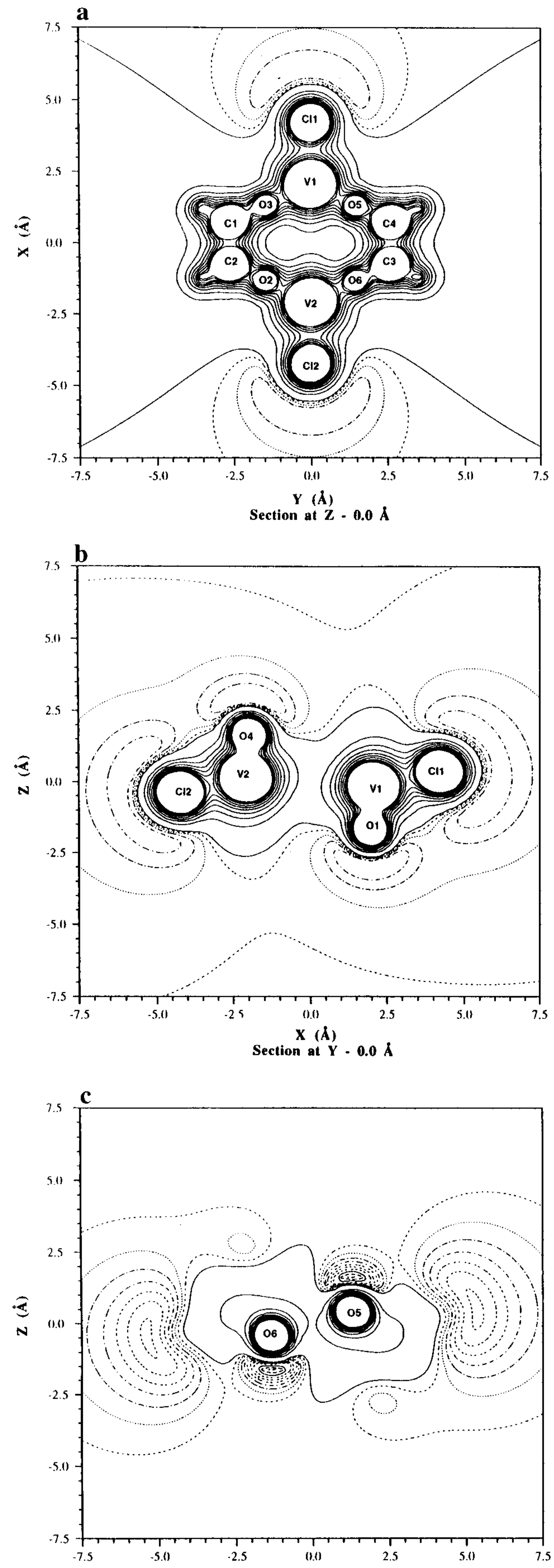

Figure 4. Electrostatic potential distribution map for compound **3** in three different planes: (a) $z = 0.0$ Å containing the inversion point of the molecule; (b) $y = 0.0$ Å; and (c) $y = 1.5$ Å. The numbering system shown in Figure 1 is employed.

Electrostatic Potential Distribution and Properties of Compound 1 Substituted with Methyl Groups. When initially deriving the structure for compound **1** from the experimental structure for compound **2**, we replaced eight methyl groups with H groups. In the following section we examine the possibility that this substitution affected the electrostatic properties of the compounds under examination. We address this point because both compounds **1** and **3** have been observed in solution,[18] whereas compound **2** does not form an observable concentration of the equivalent of compound **3** upon dissolution.[17] Furthermore, both the Thorpe−Ingold and the *gem*-dialkyl effects are strongly sensitive to these methyl groups, and it is important to establish whether the electrostatic potentials are affected by such replacement. Accordingly, two methyl groups were added to one of the carbon atoms (C_1) in compound **1** to give compound **5**, and the electrostatic distribution map of this compound was analyzed.

The HOMO and LUMO of compound **5** have electron density in a manner very similar to the HOMO and LUMO of compound **1**. The eigenvalues for the HOMO and LUMO for compound **5** −0.4363 and 0.0041 hartree, which are slightly higher in energy than the HOMO and LUMO for compound **1**. The net atomic charges in compound **5** (compared to compound **1**) increased by 0.70 (or 0.23) on the methyl group and the atomic charge decreased by 0.55 on the adjacent carbon (or increased by 0.06) as determined by SCFMEP (or the Mulliken analysis). Although the methyl group substitution affected the nature of the C−O bond, the net atomic charge on the oxygen atom only changed by 0.003 (or 0.003). The small effect on the oxygen atom is in accord with the increase by 0.06 (or decrease by 0.005) on the vanadium atom in compound **5**. Although the quantitative description may be different in calculations with an improved basis set, the observed pattern is likely to persist.

Total density maps were calculated to determine in detail whether the methyl group substitution affected the vanadium atom and the molecular density environment. Comparison of total density maps through the atoms V_1, O_3, C_1, and C_2 of both compounds **1** and **5** shows some change around C_1, the carbon atom that was replaced (Figure 5a−c), and a small change around the vanadium atom. In addition, total density maps in the C−C−O (C_2−C_1−O_3) plane (Figure 5d−f) also show some

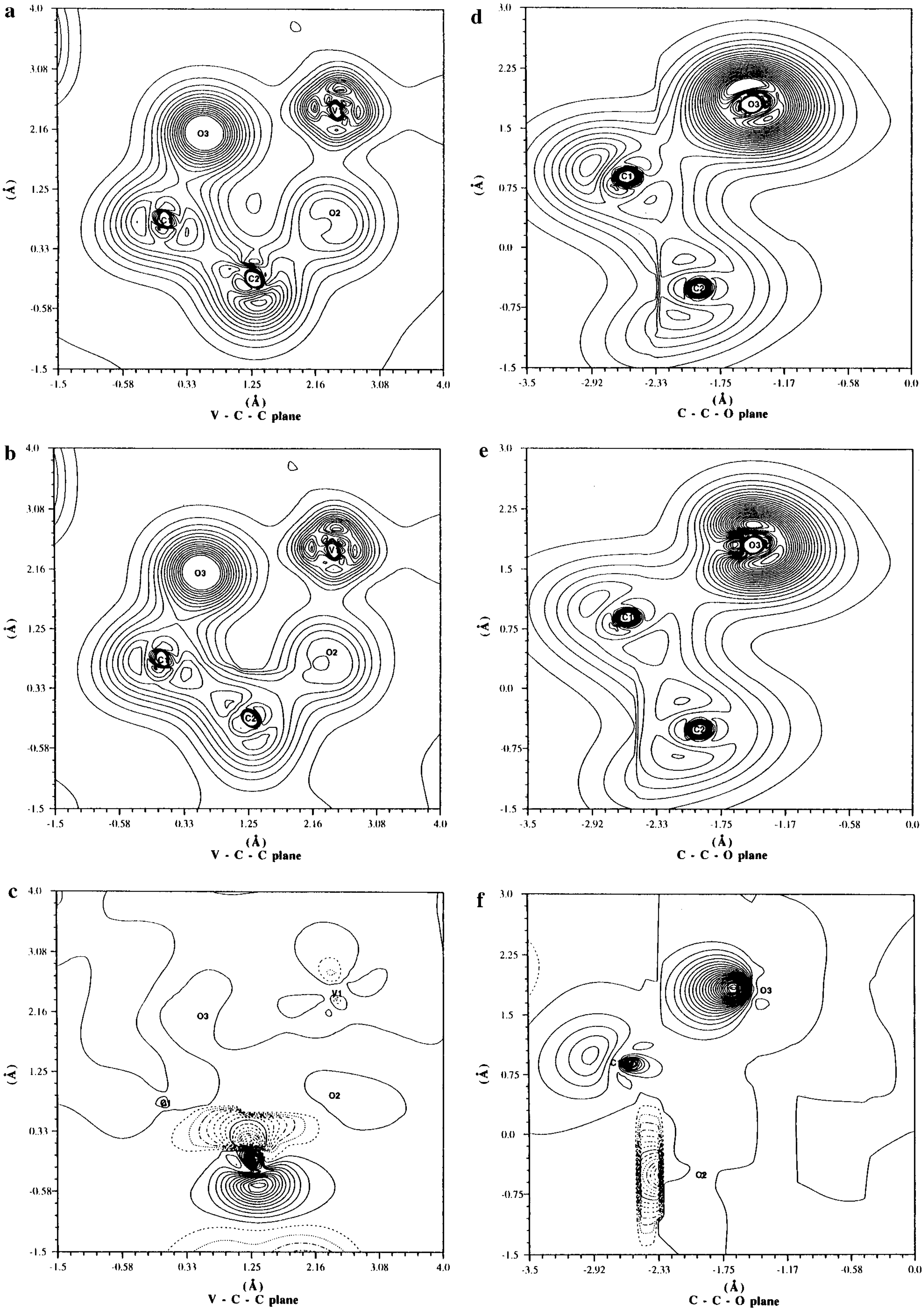

Figure 5. Comparison of the partial electron density maps for compound **1** and the tetramethyl-substituted compound (compound **5**): (a) and (b) $z = 0.0$ Å containing the inversion point of the molecule of compounds **1** and **5**, respectively; (c) difference map of (a) and (b); (d) and (e) closeups of the C−C−O ($C_2C_1O_3$) fragment in compounds **1** and **5**; (f) difference map of (d) and (e). The number system shown in Figure 1 was employed before the substitution of H_1 and H_2 (on C_1) with C_5 and C_6.

change in the neighborhood of the O_3 atom, indicating small differences in the electronics of the C_1-O_3 bond. We conclude that the replacement of the hydrogen atoms on C_1 by the methyl groups resulted in observable shifts in the saddle points of the electrostatic potential distribution, most noticeably in the region between the O_2 atom and the vanadium. However, the locations of the overall energy minima did not change significantly. Figure 5f shows the reorganization of the electrons due to the introduction of the methyl groups. The solid contours represent the area in which the electron density is higher in compound **1** than in compound **5**. The dashed contours represent the area with lower electron density in compound **1** than in compound **5**. By removing the methyl groups, we notice a difference in electron density in the bond between the C_1 carbon atom and the O_3 oxygen atom, resulting in a slightly increased density of electrons near the O_3 oxygen in compound **1**. The total density suggests that the substitution by methyl groups on compound **1** does indeed shift the electrostatic saddle points within the 10-membered ring and increase the electron density on O_3. These electrostatic differences may contribute to an increased activation barrier for the conversion between two isomers in which methyl groups replaced H atoms, perhaps in part explaining why both isomers are not observed in a solution of compounds with methyl group-substituted ligands.

Stability and Reactivity of Compounds 1−5. Compound **4** is a very polar compound as reflected by its large dipole moment. In addition, the electron affinity of the vanadium in this compound is very high; it will react with any nucleophilic site and it is a potent Lewis acid. This conclusion is confirmed by experimental data, because the dimerization product of compound **4** is the only species observed in nonpolar solvents by ^{51}V NMR spectroscopy (compound **1** decomposes in polar solvents).[18] Upon dimerization of **4** to **1**, the charge on the vanadium atom decreases, and the electron affinity of the vanadium atom decreases. Although no monomer was observed with either pinacol or ethylene glycol, one related monomer has been structurally characterized.[47] In this compound, the vanadium center was protected from nucleophilic attack by placing two phenoxy groups substituted with a *tert*-butyl group to sterically protect the vanadium.

The combination of localized strong and weak bonds in compound **1** explains some reactivity patterns in this molecule. The weak bonds in the V_2O_2 unit observed in compound **1** explain why treatment with oxygen, nitrogen, and carbon nucleophiles does not substitute the Cl atom as expected. Instead the compound decomposes. The extensive orbital mixing stabilizes the V−Cl bonds by orbital mixing far below the weak bonds in the $V_2O_2^-$ unit and is consistent with the cleavage of these bonds first. Protonation and reactions of compound **1** as a Lewis base are not likely to directly involve the V_2O_2 unit but would occur at the O_3 site. This expectation can be made because the calculations show that the triply bridged O_2 atom is not associated with an electrostatic energy minimum, in contrast to the observations in decavanadate.[34]

Comparison of compounds **1** and **4** indicates that the compound containing four-coordinate vanadium is much less stable than the compound containing five-coordinate vanadium. This is true experimentally (with the exception of the ethylene glycol compound) and according to the calculations presented here. However, the stability of compound **3** suggests that the instability of compound **4** is not simply due to the four-coordinate vanadium atom. The most stable conformation of compound **3** is a symmetrical arrangement in which stabilizing interactions between the vanadium and oxygen atoms across the ring are not enjoyed. Instead the compound is placed in a favorable staggered conformation with the chlorine atoms in an arrangement that decreases the polarity of the molecule and reduces steric interactions (see the following). Both the V−O and C−O bonds are strengthened and the charge on the vanadium atom is increased, resulting in a molecule with extensive orbital mixing and lacking the weak bonding found in the V_2O_2 unit.

The staggered, flexible, 10-membered ring, perhaps in a somewhat flattened conformation, decreases steric interactions between an axial substituent on the carbon and the chlorine atom and seems to be more sterically favored than the more congested and rigid structure containing the V_2O_2 unit. Why then is compound **2** observed when pinacol is the ligand and not the staggered 10-membered ring? If neither the geometry around the metal nor electronic effects are responsible, alternative geometric effects should be considered. The Thorpe−Ingold effect would favor decreasing the distance between the oxygen atoms in a substituted diol and, accordingly, increasing the distances between the methyl substituents on the ethylene glycol unit by decreasing the O−O distances of the C−C−O angles. The latter interactions are quite unfavorable in pinacol as reflected by the increased internal C−C bond in compound **2**. Furthermore, by examining the relevant O−O distances in compounds **1**, **3**, and **4**, we find 2.40 (exp)/2.37 (calcd) Å, 2.86 (exp)/2.90 (calcd) Å and 2.40 (calcd) Å, respectively, or expressed in terms of the C−C−O angles in compounds **1**, **3**, and **4**, we find 104.1°, 102.3° (exp)/102.2°, 102.1° (calcd), 109.8°, 109.5° (exp)/108.2°, 108.2° (calcd), and 104.6°, 104.5° (calcd), respectively. Therefore, the observed stability pattern (short O−O distance, intact V_2O_2 unit) is consistent with the Thorpe−Ingold effect.[20] The *gem*-dialkyl effect originates mainly from the population differences in conformers upon methyl substitution.[20] In ethylene glycol the energy difference between the most stable *anti* conformation and the *syn* conformation observed in compound **1** is large. As methyl groups replace H-atoms on the ethylene glycol unit, the energy difference between *anti* and *syn* conformations decreases. Accordingly, the population of the *syn* conformer, as found in compound **1**, increases upon alkyl substitution. Therefore, the observed stability pattern for compounds **1** and **3** is also consistent with the *gem*-dialkyl effect. Since both effects increase the stability of compound **1** over **3**, either or both could be important contributors to the final stability pattern. We conclude that there is no doubt that the coordination preferences are consistent with the Thorpe−Ingold and/or *gem*-dialkyl effects, but not with electrostatic effects.

The sensitivity of oxidation reactions catalyzed by vanadium oxides to various substrates is well recognized.[15] Spectroscopic studies with the thin vanadium oxide films have recently shown that the HOMO of the pseudo tetrahedral oxovanadium derivative (presumed to be the reactive center) should correctly be assigned to a nonbonding orbital with electron density on basal oxygen atoms (as opposed to electron density on the V═O oxygen atom).[40] Spectroscopic evidence with other substrates will further substantiate this hypothesis, since the possibility that structural changes affect the arrangement of the orbitals must be considered. The theoretical studies presented here, however, do provide some important information in this regard. The three oxovanadium alkoxides examined have very different geometries and coordination numbers, and despite these differences, all three oxovanadium alkoxides have HOMOs that are nonbonding orbitals with electron densities on the basal substituents. Furthermore, the studies described here provide information on the properties of compounds under consideration as catalysts for various redox reactions.[48] Modification of the Lewis acid properties of appropriate vanadium compounds could

---

(47) Toscano, P. J.; Schermerhorn, E. J.; Dettelbacher, C.; Macherone, D.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1991**, 933−934.

be of practical significance if the factors modifying these properties were better understood.[49]

Although major differences are apparent by this substitution, it is likely that some of the conclusions made in these oxovanadium chloroalkoxide studies will also apply to the vanadate esters of biological significance. Since the structural and solution chemistry of all relevant compounds is known for the series of oxovanadium chloroalkoxides, these compounds are ideal to explore the electronic properties of vanadium in comparable four- and five-coordinate compounds (reviewed in refs 9 and 50). Recent studies with the vanadium(V)−ethylene glycol complex convincingly show that a compound with geometry analogous to compound **1** is the major product in aqueous solution and thus document the appropriateness of the oxovanadium chloroalkoxides as model systems for the aqueous vanadate esters.[50] It would be very difficult to reach the same depth in the analysis of the corresponding aqueous systems at this time.

Conclusion

The small discrepancies between the optimized structures for compounds **1** and **3** with the structures obtained by X-ray crystallography attest to the ability of the (12s7p5d)/[5s3p2d] basis set to generate reliable geometries of oxovanadium chloroalkoxides even in the absence of diffuse and/or polarization functions. Electrostatic potential and other calculations were used to characterize the electronic properties of three molecules, including one mononuclear and two dinuclear cyclic oxovanadium chloroalkoxides. The dinuclear compounds were previously characterized experimentally both in the solid state and in solution, whereas the mononuclear compound has not been observed directly. From these calculations it appears that the reactivity of the monomeric unit originates from its electrostatic properties rather than from the coordination number of the vanadium atom. Although electrostatic properties are instrumental for both the stability and reactivity, neither the electrostatic properties of the metal atom nor the steric bulk around the metal atom was, at this level of theory, found to determine the coordination number of the metal in each oxovanadium chloroalkoxide. Instead, the subtle geometric effects in ligand geometry induced by the Thorpe−Ingold and/or *gem*-dialkyl effects are consistent with the observed coordination number of the vanadium atom in these types of compounds.

Acknowledgment. The calculations have been performed at CIRCE (CNRS) on an IBM 3090 computer and at Eagan on a Cray YMP16-C90 computer. We thank the Direction des Recherches, Etudes et Techniques, for financial support (decision no. 87246) and the National Institutes of Health (to D.C.C.), the Groupement scientifique Model'isation Mol'eculaire CNRS IBM, and C Henriet (Cray Research France) for computing resources. We also thank Drs. Jeffrey M. Stryker and Christopher R. Roberts for stimulating discussions probing these results.

Supporting Information Available: Tables of exponents and contraction coefficients used for the basis sets for vanadium, oxygen, carbon, chloride, and hydrogen (Table S1) and the total energies for compound **1** at selected basis sets (Table S2) (5 pages). Ordering information is given on any current masthead page.

IC9601706

---

(48) Nugent, W. A.; RajanBabu, T. V.; Burk, M. J. *Science* **1993**, *259,* 479−483.

(49) Viet, M. T. P.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30,* 3026−3032.

(50) Ray, W. J., Jr.; Crans, D. C.; Zheng, J.; Burgner, J. W., II; Deng, H.; Mahroof-Tahir, M. *J. Am. Chem. Soc.* **1995**, *117,* 6015−6026.