peak tops are sampled in ω (0.6° each side of Kα). One quadrant of data was collected *h*,*k*,±*l* out to 45° in 2θ. The intensities of 2 standards were measured after every 98 reflections and showed no significant decay during the data collection period. The data was collected on a Syntex (Nicolet) P2₁ diffractometer equipped with a graphite-crystal monochrometer.

Solution and Refinement of the Structure. The structure determination and refinements were carried out with the Structure Determination Package[39] running on a PDP 11/34a computer. Phases provided by MULTAN were used to solve the structure with difference Fourier techniques used to locate the atoms not found in the *E* map. Isotropic refinement of the phenyl rings and anisotropic refinement of all other non-hydrogen atoms led to $R_1 = 0.061$, $R_2 = 0.064$ with a GOF of 2.4. Analysis of the weighting scheme and peak profiles lead to downweighting the more intense reflections by increasing the data stability constant $(p)^{40}$ from 0.03 to 0.06. The $I/\sigma(I)$ limit was set to 2.5 in order to maintain at least a 7:1 data to parameter ratio. All non-hydrogen atoms were refined isotropically for four cycles with hydrogen atoms added as fixed contributions to F_c at calculated positions. This led to the final tabulated results with $R_1 = 0.044$, $R_2 = 0.052$ and a goodness of fit value of 1.1.

Conclusions

The reactions of CO with $Pd(NO_2)_2L_2$ provide a general and useful synthetic method for preparing Pd(0) carbonyl clusters in high yield from air-stable, conveniently available starting materials. The fact that several different tertiary phosphine complexes undergo the same reaction allows the Pd(0) cluster to be derivatized. Other phosphine ligands such as PEt_2Ph led to the formation of unique Pd(I) dimers.

(39) Structure Determination Package (B. A. Frenz and Associates, Inc., College Station, TX 77840, and Enraf-Nonius, Delft, Holland).

(40) $w = 1/\sigma(F_o)^2 = 4F_o^2/[\sigma(F_o^2)^2 + (pF_o^2)^2]$.

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Multiple Bonds between Vanadium Atoms

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Opportunities are considered for extending the type of chemistry of vanadium(II) in which multiple bonds are formed between metal atoms in light of available experimental facts and molecular orbital calculations. The bond (2.200 Å) in $V_2(DMP)_4$ (DMP = 2,6-dimethoxyphenyl) is formulated as a $\sigma^2\pi^2\delta^2$ triple bond in an edge-sharing bioctahedron. It is argued that in some $V_2(XYZ)_4$ molecules $\sigma^2\pi^4$ triple bonds shorter than 2.20 Å should be stable provided the XYZ^- ligands are chosen to obviate rearrangement (such as that which occurs with $V_2(DMP)_4$) or further reaction. As a model system for both Fenske–Hall and Hartree–Fock calculations pertaining to $V_2(XYZ)_4$ molecules, $V_2(O_2CH)_4$ has been used. The two computations give orbital energies in excellent agreement. The calculations clearly indicate the stability of a $\sigma^2\pi^4$ V≡V bond. The failure of synthetic efforts to prepare $V_2(O_2CR)_4$ molecules is probably due to the even greater stability of $[V_3(\mu_3-O)(O_2CR)_6L_3]^n$ ($n = 0, 1+$) species. It is suggested that other XYZ ligands should be able to give isolable $V_2(XYZ)_4$ molecules. The bonding in the compound $V_2(PMePh_2)_4$-$(H_2ZnH_2BH_2)_2$ is analyzed, and it is shown that a change in P–V–P bond angles could lead to the formation of a quadruple $(\sigma^2\pi^4\delta^2)$ V–V bond.

Introduction

The ability of most of the d-block transition metal atoms to form metal–metal bonds of orders 2–4, based primarily on the overlap of d orbitals, is now well established.[2] If one examines the way in which the propensity for forming such bonds varies from element to element, one of the most conspicuous and important features of the pattern is that few such bonds are formed by the elements of the 3d series, i.e., Sc–Cu. Only chromium is known to form an extensive series of compounds, namely, those in which quadruple bonds occur.[2-4]

A question that naturally arises is whether the absence of compounds containing strong M–M bonds between atoms of other 3d metallic elements is to be ascribed to the inherent inability of these elements to form such compounds or simply to the failure of chemists to devise reactions and conditions suitable for isolating them. The answer to this question can be approached by both experimental and theoretical means. It is recognized, of course, that neither approach will ever lead to a proof of the negative, i.e., to proof that such bonds cannot under any circumstances exist. What we can hope to do by experiment is to achieve a proof of the positive, that is actually to isolate one or more such compounds, and thus show definitively that they can exist. This will always be the ultimate goal. In an effort to achieve it, however, we can seek guidance from theory as to the types of compounds that it is realistic to expect.

In this paper we shall do the following things: (1) We shall review some experimental facts that lead to the conclusion that vanadium is a 3d metal that holds promise of affording compounds with multiple metal–metal bonds. (2) We shall report a Hartree–Fock calculation on a model divanadium compound, V_2-$(O_2CH)_4$, which provides further support for optimism regarding vanadium. (3) We shall relate the results of this calculation to some practical, experimental considerations. (4) We shall show that Fenske–Hall calculations on $V_2(O_2CH)_4$ give results in good

(1) (a) Texas A&M University. (b) Technical University of Denmark.

(2) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(3) Cotton, F. A. Wang, W. *Nouv. J. Chim.* **1984,** *8,* 331.

(4) Ketkar, S. N.; Fink, M. *J. Am. Chem. Soc.* **1985,** *107,* 338.

agreement with the Hartree–Fock results. (5) We shall use Fenske–Hall calculations to analyze the bonding in V_2-$(PMePh_2)_4(H_2ZnH_2BH_2)_2$, a recently reported compound, and thereby show that if the structure of this molecule could be altered so as to give a more linear P–V–P group, a quadruple bond would result.

Background Concerning V–V Bonds

There are several indications in the literature that vanadium is probably the next best candidate, after chromium, for forming strong (i.e., multiple) metal–metal bonds. We turn first to the available information on diatomic metal molecules, M_2. There have been both theoretical[5] and experimental[6] studies of these molecules for the 3d metals, from which it is clear that only V_2 and Cr_2 are strongly d-orbitally bonded. The Cr_2 molecule has a sextuply bonded $^1\Sigma_g^+$ ground state, with an internuclear distance of 1.68 Å. The V_2 molecule[7] has a $^3\Sigma_g^-$ ground state with a pentuple bond and an internuclear distance of 1.77 Å. If this similarity in the characteristics of their M_2 molecules for chromium and vanadium implies broader similarities, a search for triply bonded V_2^{4+} compounds comparable to the quadruply bonded Cr_2^{4+} compounds would seem worthwhile.

It happens that the literature already records one pair of compounds that might have been expected to provide the appropriate analogy, namely $V_2(DMP)_4$[8] and $Cr_2(DMP)_4$,[9] where DMP is an ad hoc abbreviation for the 2,6-dimethoxyphenyl group (I). However, the two compounds do not have the same structure.

MeO⎯◯⎯OMe

I
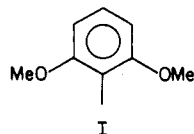
The chromium compound has a structure of the type that is typical for $M_2(XYZ)_4$ molecules, where XYZ is used as a general symbol of a bridging bidentate ligand with a three-atom chain. The $Cr_2(DMP)_4$ structure can be represented as II; all four of the DMP
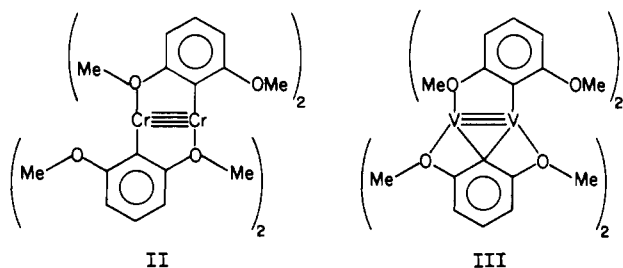
II   III

ligands have the same relationship to the dimetal unit. In V_2-$(DMP)_4$ only two of the ligands (which are trans to each other) have this relationship, while the other two (also, of course, trans to each other) have a different relationship, as shown in III. In the original report of this $V_2(DMP)_4$ structure, it was suggested that, as an approximation, the difference in the two ligand arrangements could be neglected and the V≡V bond regarded as a $\sigma^2\pi^4$ type triple bond, analogous to the $\sigma^2\pi^4\delta^2$ quadruple bond in the $Cr_2(DMP)_4$ molecule, minus the two δ electrons. We now propose to abandon this point of view and advocate a different
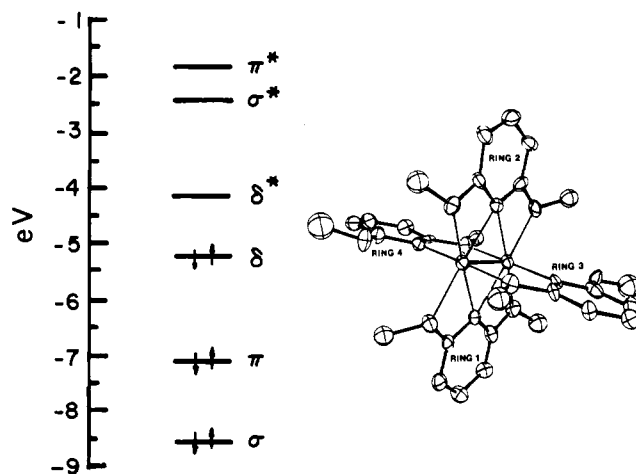

Figure 1. Molecular orbital energy diagram for those orbitals mainly concerned with V–V bonding in $V_2(DMP)_4$, based on a Fenske–Hall calculation.

way of formulating this particular V≡V bond that is in full accord with the details of the ligand arrangement.

When viewed in the proper perspective, as shown schematically in IV, the $V_2(DMP)_4$ molecule is really an example of an edge-sharing bioctahedron, with two phenyl carbon atoms serving as

IV
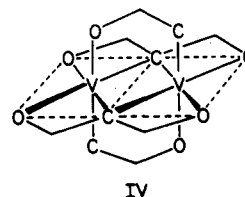
the bridging atoms. From this point of view, the V≡V bonding must be formulated as a $\sigma^2\pi^2\delta^2$ type of bond, in accord with the general qualitative ideas that are well established for edge-sharing bioctahedra.[10] The Fenske–Hall approximation[11] to the Hartree–Fock method has been applied to this molecule, using the reported structure parameters, with the results summarized in Figure 1 for the orbitals that are principally concerned with V–V bonding. The σ and π bonds are rather strong, probably comparable to those one would expect in a $Cr_2(DMP)_4$ type of molecule, but there is only one rather than two such π bonds. Instead of a second π bond there is a δ bond that is relatively weak. This raises the question of why $V_2(DMP)_4$ has the structure it does when it could presumably achieve stronger V≡V bonding by adopting the $Cr_2(DMP)_4$ structure.

Presumably, the structure actually adopted by $V_2(DMP)_4$ is favored, despite the sacrifice of a π bond in favor of a weaker δ bond, by increases in metal–ligand bond energies. In the structure adopted there are 12 metal–ligand bonds, as opposed to only eight in the $Cr_2(DMP)_4$ type structure. Moreover, the octahedral coordination about each metal atom is in keeping with the characteristic tendency of d^3 transition-metal ions to form thermodynamically and kinetically stable octahedral complexes.

Some Observations on $V_2(PMePh_2)_4(H_2ZnH_2BH_2)_2$

In 1983 Caulton and co-workers[12] reported the preparation and structural characterization of a peculiar molecule having the structure shown schematically as V. The formal oxidation state of the vanadium atoms is +1, and the V–V distance is 2.400 (2) Å. It was suggested that the V–V bond order is 2 and that the failure of the two d^4 vanadium(I) atoms to form a quadruple bond could be attributed to the large V–V–P angles (i.e., P–V–P angles ≪180°) in the planar V_2P_4 unit. It was proposed that this led

(5) Representative and recent calculations on various M_2 molecules: (a) Walch, S. P.; Bauschlicher, C. W.; Roos, B. O.; Nelin, C. J. *Chem. Phys. Lett.* **1983**, *103*, 1751 (V_2). (b) Kok, R. D.; Hall, M. B. *J. Phys. Chem.* **1983**, *87*, 715 (Cr_2). (c) Shim, I.; Gingerich, K. A. *J. Chem. Phys.* **1982**, *77*, 2490 (Fe_2). (d) Shim, I.; Gingerich, K. A.; *J. Chem. Phys.* **1983**, *78*, 5693 (Co_2). (e) Shim. I.; Johansen, H.; Dahl, J. P. *Int. J. Quantum Chem.* **1979**, *15*, (311). (f) Shim, I.; Gingerich, K. A. *J. Chem. Phys.* **1983**, *79*, 2903.
(6) Morse, M. D.; Smalley, R. E. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 228.
(7) Langridge-Smith, P. R. R.; Morse, M. D.; Hansen, G. P.; Smalley, R. E.; Merer, A. J. *J. Chem. Phys.* **1984**, *80*, 595.
(8) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886.
(9) Cotton, F. A.; Koch, S. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2087.

(10) Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.
(11) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.
(12) Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 6163.

V, P = PMePh$_2$
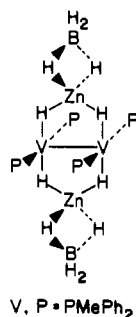
to destabilization of one of the potentially π-bonding V–V molecular orbitals to the extent that it is raised to an energy above both the δ and δ^* orbitals. This then leads to an electron configuration $\sigma^2\pi^2\delta^2\delta^{*2}$, corresponding to a double bond. This analysis of the bonding seemed to us to be qualitatively very persuasive. We wondered whether it, and some inferences that could be drawn from it, would be supported by calculations at the Fenske–Hall level.

The results of the Fenske–Hall calculations are shown in Figure 2. The phosphine ligands have been modeled by PH$_3$ groups, but otherwise the actual molecular structure has been used. The results entirely support Caulton's suggestion. We then extended the calculation to a hypothetical case in which the P–V–P groups were made linear. It was expected that this would allow the formation of a second V–V π bond, and it can be seen in Figure 2 that this is exactly what happens. It is very likely that this calculation underestimates the increase in V–V bonding that would actually occur if the P–V–P groups could be made linear (or, at least, more nearly linear) since the additional V–V π bond would be expected to shorten the V–V distance and thus increase the strength of all components of the resulting $\sigma^2\pi_1^2\pi_2^2\delta^2$ quadruple bond. Judging from the 2.20-Å distance for the triple bond in V$_2$(DMP)$_4$, a distance shorter than 2.20 Å would be expected.

In practice, of course, the opening of the P–V–P angles toward linearity is opposed by the repulsive forces between the substituents on the phosphorus atoms. This suggests that replacement of the four phosphine ligands with two neutral XYZ ligands, which would be compatible with the existence of linear L–V–L angles, a quadruply bonded divanadium compound might become stable. Since a number of suitable XYZ ligands are known, an experimental effort in this direction would seem worthwhile.

Calculations on V$_2$(O$_2$CH)$_4$

To gain more direct insight into the possibility of developing strong metal–metal bonds, probably V≡≡V bonds, in the framework of a conventional V$_2$(XYZ)$_4$ type structure, we have carried out calculations on the model system V$_2$(O$_2$CH)$_4$, employing both the Hartree–Fock–Roothaan (HFR) formalism[13] in its complete form and the Fenske–Hall[11] approximation thereto.

HFR Method. (1) Basis Sets. The basis sets consisted of Gaussian type functions. For the V atom we have utilized a modified version of the basis optimized by Huzinaga[14] for the ^{4}F(3d)^3(4s)^2 term. In order to describe the 4p orbital, we extend Huzinaga's basis by addition of two p functions with exponents 0.17 and 0.07, and we also added a diffuse d function with exponent 0.11. The exponents of the additional functions have been determined by a method described by Raffenetti.[15] Furthermore, the exponents of the most diffuse s functions have been altered from 0.091 315 980 and 0.035 126 260 to 0.16 and 0.055, respectively. Whereas the maxima of the original functions are at 2.34 and 3.77 au, the maxima of the modified functions are at 1.77 and 3.02 au. We believe the alterations performed result in a better description of the valence region of the molecule. The primitive basis (14s,11p,6d) was contracted to (8s,6p,3d) by using a segmented contraction scheme. The coefficients of the contracted functions have been derived from calculations on the
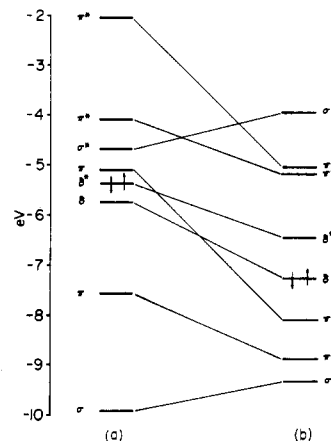

Figure 2. Orbital energy levels for a V$_2$(PH$_3$)$_4$(H$_2$ZnH$_2$BH$_2$)$_2$ molecule calculated for a V–V distance of 2.400 Å with (a) the P–V–P angles equal to 106.4° and (b) the P–V–P angles equal to 180°.

Table I. Total Energies (au) Derived in Hartree–Fock Calculations Using Contracted Gaussian-Type Basis Sets

atom	term	basis set	energy
V	^{4}F(3d)^3(4s)^2	(14s,11p,6d)–(8s,6p,3d)	−942.837 840
O	^{3}P(2s)^2(2p)^4	(9s,5p)–(4s,2p)	−74.800 290
C	^{3}P(2s)^2(2p)^2	(9s,5p)–(4s,2p)	−37.685 240
H	^{2}S(1s)^1	(4s)–(2s)	−0.499 277

Table II. Splitting of Atomic Orbitals of V$_2$(O$_2$CH)$_4$ due to the D_{4h} Symmetry

atom	orbital	D_{4h} symmetry
V	s	$a_{1g} + a_{2u}$
	d_{z^2}	$a_{1g} + a_{2u}$
	d_{xz}, d_{yz}	$e_u + e_g$
	$d_{x^2-y^2}$	$b_{2g} + b_{1u}$
	d_{xy}	$b_{1g} + b_{2u}$
O	s	$a_{1g} + e_u + b_{1g} + a_{2u} + e_g + b_{2u}$
	p_x, p_y	$a_{1g} + e_u + b_{1g} + b_{2g} + a_{2g} + a_{2u} + e_g + b_{2u} + b_{1u} + a_{1u}$
	p_z	$a_{1g} + e_u + b_{1g} + a_{2u} + e_g + b_{2u}$
C	s	$a_{1g} + e_u + b_{1g}$
	p_x, p_y	$a_{1g} + e_u + b_{1g} + b_{2g} + a_{2g}$
	p_z	$a_{2u} + e_g + b_{2u}$
H	s	$a_{1g} + e_u + b_{1g}$

^{4}F(3d)^3(4s)^2 term of the V atom. In the contracted basis the 3d orbital is represented by a triple-ζ function, whereas all other orbitals including the 4p orbital are represented by double-ζ functions. For the atoms O, C, and H we also utilized basis sets published by Huzinaga.[16] The primitive sets for O and C (9s,5p) were contracted to (4s,2p), and for H (4s) was contracted to (2s). In Table I we present the total energies of the V, O, C, and H atoms.

(2) Molecular Geometry. Since the molecule V$_2$(O$_2$CH)$_4$ is not yet known experimentally, we have assumed that the molecule has D_{4h} symmetry and we have chosen the following set of molecular parameters: V–O = 2.00 Å; C–O = 1.26 Å; C–H = 1.084 Å; V–V = 2.20 Å; all angles about C = 120°.

(3) Molecular Calculations. When the calculations were performed, the integrals were computed with the program MOLECULE[17] and for the HFR calculations per se we have utilized the ALCHEMY program system.[18] The primitive basis consisted of 470 Gaussian-type functions contracted to 216 functions. This basis set is believed to be the largest used in calculations on a molecule of this type. The molecule was placed in a coordinate

(13) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.
(14) Huzinaga, S. *J. Chem. Phys.* **1977**, *66*, 4245.
(15) Raffenetti, R. C. J. *J. Chem. Phys.* **1973**, *58*, 4452.

(16) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(17) Almlöf, J. In "Proceedings of the Second Seminar on Computational Problems in Quantum Chemistry", Max-Planck Institute, Munich, 1973; p 14.
(18) Bagus, P. S.; Liu, B.; Yoshimine, M.; McLean, A. D. "ALCHEMY Program System"; IBM Research Laboratory: San Jose, CA.
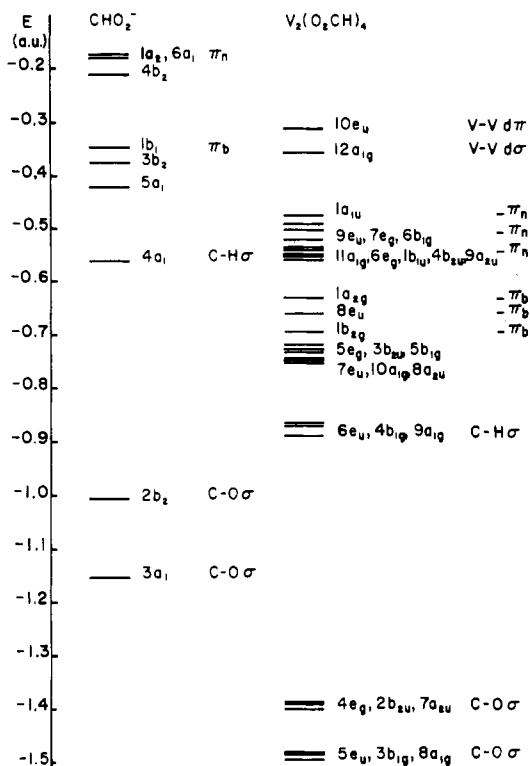
Figure 3. Orbital energies (au) resulting from Hartree–Fock calculations on the formate ion, HCO_2^-, and $V_2(O_2CH)_4$, with a $d\sigma^2 d\pi^4$ configuration for the latter.

Table III. Splitting of Atomic Orbitals of the Formate Ion due to the C_{2v} Symmetry

atom	orbital	C_{2v} symmetry	atom	orbital	C_{2v} symmetry
C	$s;p_x$	a_1	O	$s;p_x,p_y$	$a_1 + b_2$
	p_y	b_1		p_z	$b_1 + a_2$
	p_z	b_2	H	s	a_1

system with its origin at the midpoint of the V–V bond, the z axis collinear with the V–V bond. The planes forming angles of 45° with the xz plane were chosen to contain the four formate bridges. The classification of the atomic orbitals in D_{4h} symmetry is shown in Table II.

For comparison we also carried out calculations on an isolated formate ion having geometry identical with one of the bridges in the $V_2(O_2CH)_4$ molecule. The formate ion has C_{2v} symmetry, and it was placed in the xz plane with the C atom at the origin and the H atom on the x axis. In Table III we show the classification of the atomic orbitals in C_{2v} symmetry.

All contour plots have been performed with use of a program especially designed for contour plotting of orbitals, densities, and electrostatic potentials.[19]

(4) Results. In Figure 3 we have depicted the orbital energies of the valence orbitals of both the $V_2(O_2CH)_4$ molecule and the formate ion. Numerical values for the $V_2(O_2CH)_4$ molecule are listed in Table IV. Apart from a general shift of the orbital energies, the orbitals of the formate ions can easily be identified among the orbitals of the complex. Thus, the two lowest lying groups of orbitals in $V_2(O_2CH)_4$ at about −1.5 and −1.4 au correspond to the $3a_1$ and the $2b_2$ orbitals of the formate ion, and they give rise to the σ bonds between the C and the O atoms. A group of orbitals at about −0.9 au corresponds to the $4a_1$ orbital of the formate ion, and the σ bonds between the C and the H atoms of the formate bridges are primarily due to these orbitals. The two highest lying orbitals in $V_2(O_2CH)_4$, which have no analogue in the HCO_2^- groups, are the orbitals responsible for the bonding between the two V atoms. Among the remaining orbitals (between −0.4 and −0.8 au) are those that account for

(19) Johansen, H., private communication.

Table IV. Orbital Energies, IP's (Koopmans' Theorem), and Orbital Characters for $V_2(O_2CH)_4$ from Hartree–Fock–Roothan (HFR) and Fenske–Hall (FH) Calculations

orbital	energy, au HFR	energy, au FH	IP, eV HFR	orbital char V–V	orbital char HCO_2^- orbital parentage
$10a_{2u}$	0.0669	−0.0599		$d\sigma^*$	
$2b_{2g}$	0.0521	−0.2415		$d\delta$	
$8e_g$	0.0384	−0.1008		$d\pi^*$	
$10e_u$	−0.3136	−0.2978	8.5	$d\pi$	
$12a_{1g}$	−0.3532	−0.3605	9.6	$d\sigma$	
$1a_{1u}$	−0.4791	−0.5113	13.0		$1a_2$
$9e_u$	−0.4924	−0.5171	13.4		$6a_1$
$7e_g$	−0.5041	−0.5224	13.7		$1a_2$
$6b_{1g}$	−0.5212	−0.5735	14.2		$6a_1$
$11a_{1g}$	−0.5389	−0.5531	14.7		$6a_1$
$6e_g$	−0.5402	−0.5224	14.7		$4b_2$
$1b_{1u}$	−0.5498	−0.5552	15.0		$1a_2$
$4b_{2u}$	−0.5500	−0.5182	15.0		$4b_2$
$9a_{2u}$	−0.5588	−0.5244	15.2		$4b_2$
$1a_{2g}$	−0.6322	−0.7033	17.2		$1b_1$
$8e_u$	−0.6618	−0.7107	18.0		$1b_1$
$1b_{2g}$	−0.6954	−0.7165	18.9		$1b_1$
$5e_g$	−0.7190	−0.6936	19.6		$3b_2$
$3b_{2u}$	−0.7278	−0.7482	19.8		$3b_2$
$5b_{1g}$	−0.7335	−0.7568	20.0		$5a_1$
$7e_u$	−0.7480	−0.7402	20.4		$5a_1$
$10a_{1g}$	−0.7494	−0.7522	20.4		$5a_1$
$8a_{2u}$	−0.7540	−0.7365	20.5		$3b_2$
$6e_u$	−0.8663	−0.9296	23.6		$4a_1$
$4b_{1g}$	−0.8727	−0.9377	23.8		$4a_1$
$9a_{1g}$	−0.8890	−0.9336	24.2		$4a_1$
$4e_g$	−1.3865	−1.3792	37.7		$2b_2$
$2b_{2u}$	−1.3884	−1.3763	37.8		$2b_2$
$7a_{2u}$	−1.3971	−1.3751	38.0		$2b_2$
$5e_u$	−1.4835	−1.4872	40.4		$3a_1$
$3b_{1g}$	−1.4844	−1.4629	40.4		$3a_1$
$8a_{1g}$	−1.4948	−1.4756	40.7		$3a_1$

Table V. Charge in the V Orbitals due to Back-Donation of Electrons from the Formate Ions to One of the V Atoms

	σ	π	δ
d	0.05	0.11	0.43
p	0.04	0.48	
s	0.25		

C–O π electrons, O lone-pair electrons, and V–O bonding electrons. The latter two types of orbitals are very mixed and cannot be individually identified. The details of this correspondence is revealed in Table IV where we also present the vertical ionization potentials (i.e., according to Koopmans' theorem[20]) for the high-lying orbitals of the $V_2(O_2CH)_4$ molecule.

The bonding between the V and the O atoms of the $V_2(O_2CH)_4$ molecule, which cannot be associated with any specific orbitals, is established through donation of charge from the formate ions into especially the $d\delta$, the $p\pi$, and the $s\sigma$ orbitals of the V atoms as shown in Table V. This donation of charge contributes to the splittings of the orbitals of $V_2(O_2CH)_4$, corresponding to the specific orbitals of the formate ion. For some of the orbitals the donation causes the orbitals of b symmetry to lie below those of e symmetry despite the larger number of angular nodes around the z axis in the former.

(5) Conclusions. The Hartree–Fock calculation indicates that the bond between the vanadium atoms is a triple bond due primarily to the molecular orbitals $12a_{1g}$ and $10e_u$. It can be designated a $\sigma^2\pi^4$ bond in the same way as the triple bonds in such species as $Mo_2(OR)_6$ or $[Mo_2(HPO_4)_4]^{2-}$ are so described. In Table VI the Mulliken populations of the $12a_{1g}$ and $10e_u$ orbitals are presented, showing that these are, indeed, of mainly d character. They are very well localized, with 95% of the $d\pi$ and 98%

(20) Koopmans, T. A. *Physica* **1933**, *1*, 104.

Table VI. Mulliken Population Analyses of the V–V Bonding Orbitals of $V_2(O_2CH)_4$ by Hartree–Fock–Roothan (HFR) and Fenske–Hall (FH) Calculations at 2.20 Å

| | atomic populn V | | overlap populn V–V | | orbital anal. | | | | | |
| | | | | | s | | p | | d | |
orbital	HFR	FH	HFR	HF	HFR	FH	HFR	FH	HFR	FH
$10e_u \sim d\pi$	1.74	1.80	0.57	0.46	0.00	0.00	0.04	0.001	1.86	1.92
$12a_{1g} \sim d\sigma$	0.84	0.71	0.27	0.28	0.14	0.24	0.04	0.036	0.80	0.66
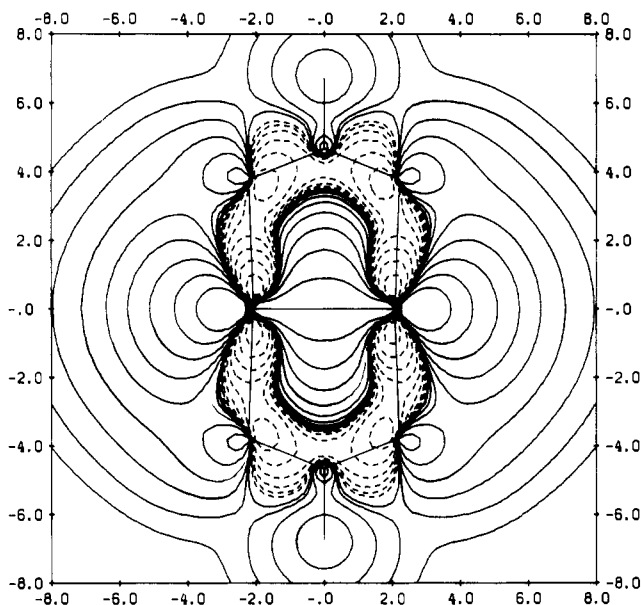
Figure 4. Contour plot of the $12a_{1g}$ (V–V dσ) orbital of $V_2(O_2CH)_4$ in a plane containing two formate bridges and the two vanadium atoms. Dashed lines indicate negative values. The lowest contour value is 6.25 × 10^{-4} e/au³, and adjacent contours differ by a factor of 2.
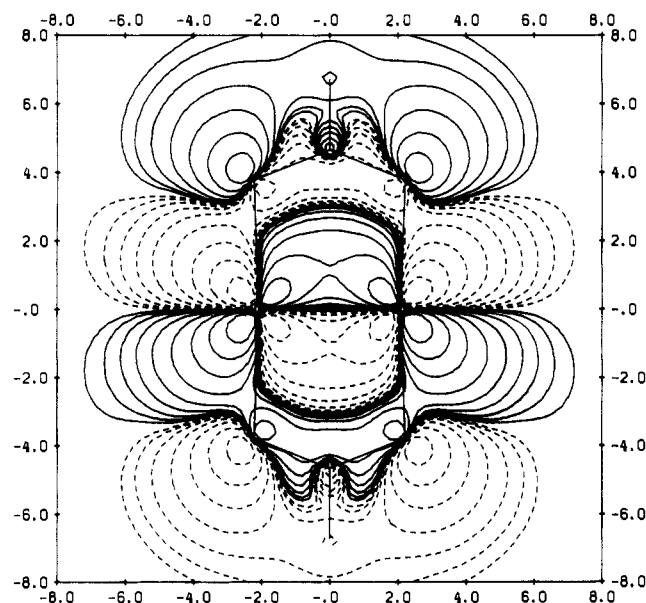
Figure 5. Contour plot of the $10e_u$ (V–V dπ) orbital of $V_2(O_2CH)_4$ in the same plane as in Figure 4 and with the same choice of contour values.

of the dσ orbitals on the V_2 unit. Figures 4 and 5 show contour plots of these orbitals. It is clear that the σ and π orbitals show their provenance in overlapping pairs of vanadium d_{z^2} and d_{xz} (or d_{yz}) atomic orbitals.

The atomization energy of the $V_2(O_2CH)_4$ molecule is 28.68 eV. Relative to two V^{2+} ions and four HCO_2^- ions, the sum of the bond energies is 35.82 eV. This indicates that the $V_2(O_2CH)_4$ molecule should be stable in the triple-bonded configuration.

One other aspect of the $V_2(O_2CH)_4$ calculation was examined in view of previous experience with the $Cr_2(O_2CH)_4$ calculations.

Table VII. Energies and Energy Differences for Several V–V Configurations for the $V_2(O_2CH)_4$ Molecule

config'n	energy, au	energy above lowest config'n, eV
$\sigma^2\delta^2\delta^{*2}$	−2637.936 04	
$\sigma^2\pi^4$	−2637.870 25	1.79
$\sigma^2\delta^2\sigma^{*2}$	−2637.813 04	3.25
$\pi^4\delta^2$	−2637.700 86	6.40

Table VIII. Gross Atomic Charges (au) Resulting from Mulliken Population Analyses of HF Calculations for the $V_2(O_2CH)_4$ Molecule and the Formate Ion

| | molecule | | | molecule | |
atom	$V_2(O_2CH)_4$	$CHOO^-$	atom	$V_2(O_2CH)_4$	$CHOO^-$
V	0.81		C	0.45	0.25
O	−0.50	−0.58	H	0.14	−0.08

Hartree–Fock calculations on the $Cr_2(O_2CH)_4$ molecule[21–23] have shown that an electronic state based on the nonbonded $\sigma^2\sigma^{*2}\delta^2\delta^{*2}$ configuration has a lower energy (in the HF approximation) than can be obtained by using the quadruple-bond configuration $\sigma^2\pi^4\delta^2$ (except at internuclear distances too short to be pertinent). On this basis we considered it worthwhile to test several other less strongly bonded configurations for $V_2(O_2CH)_4$. Altogether, four configurations have been studied, and their energies are listed in Table VII. The single-bond configuration, $\sigma^2\delta^2\delta^{*2}$, leads to a lower energy, by 1.79 eV. However, we are confident that a triple bond based on the $\sigma^2\pi^4$ configuration is a proper description of the ground state of this molecule. The lower total energy of the singly bonded molecule is presumably due to lower correlation energy in that configuration, as indicated in the deformation density maps for the two states, which we shall now discuss.

Figures 6 and 7 show deformation densities for the triply and singly bonded molecules. These are derived from the molecular electron density distributions by subtracting the superpositioned spherically averaged atomic charge densities. It is evident that for the singly bonded molecule the buildup of electron density occurs in distinct regions of space, whereas for the triply bonded molecule buildup occurs principally between the two vanadium atoms. This would certainly imply that the correlation energy must be larger for the triply bonded than for the singly bonded molecule. Even though the correlation problem certainly cannot be considered negligible for $V_2(O_2CH)_4$, it should be appreciably less severe than for $Cr_2(O_2CH)_4$ where there are eight electrons in the intermetal region. We therefore believe that a Hartree–Fock calculation, as we use it, is more reliable here than in the chromium case.

The charge distribution given by the triply bonded state is summarized in Table VIII. The charge on the HCO_2^- ion is reduced from −1.00 to −0.41 when it forms part of the $V_2(O_2CH)_4$ molecule, and the charge on the V_2^{4+} unit is reduced to +0.81 per metal atom.

Finally, some comment on the choice of a 2.20-Å V–V bond length for the calculation is appropriate. This choice was made on the basis of the observed value in $V_2(DMP)_4$ at a time when

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(22) Guest, M. F.; Garner, C. D.; Hillier, I. H.; Walton, I. B. *J. Chem. Soc., Perkin Trans. 2* **1978**, *74*, 2092.

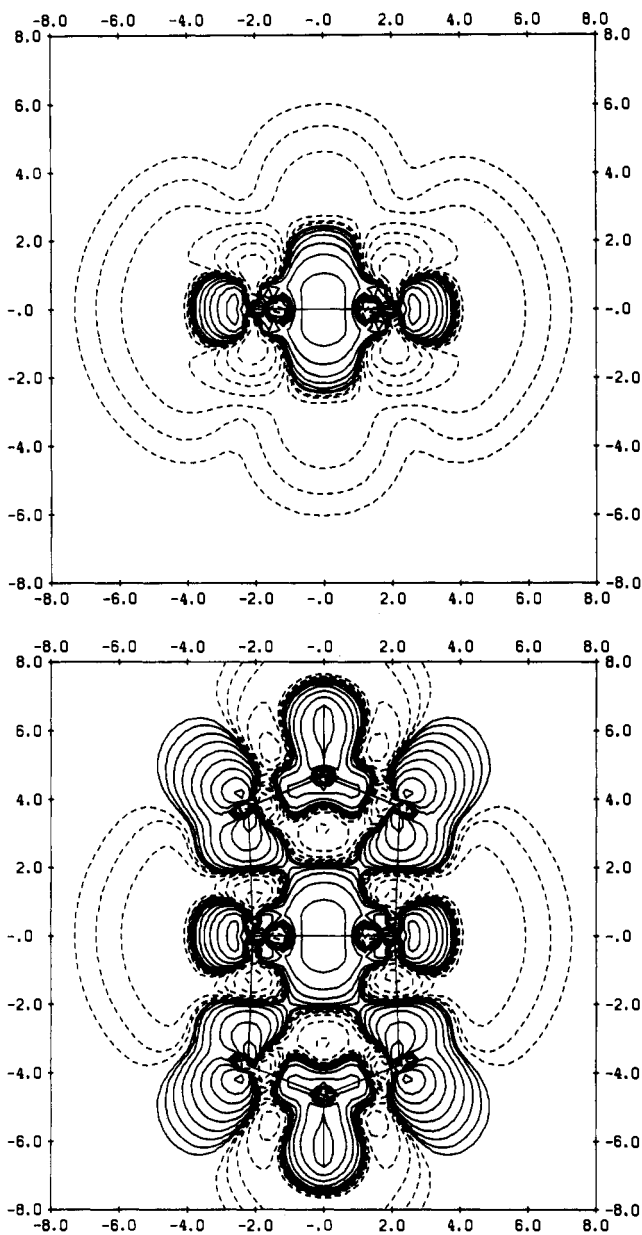(23) Bernard, M. *J. Am. Chem. Soc.* **1978**, *100*, 2354.

Figure 6. Deformation density maps for the molecular electron distribution derived from the triply bonded, $\sigma^2\pi^4$ state of $V_2(O_2CH)_4$: (lower plot) in the plane of a pair of O_2CH groups; (Upper plot) in a plane at 45° to the lower plot.

Figure 7. Deformation density maps for the molecular electron distribution derived from the singly bonded, $\sigma^2\delta^2\delta^{*2}$ state of $V_2(O_2CH)_4$: (lower plot) in a $V_2(O_2CH)_2$ plane; (upper plot) in a plane at 45° to the lower plot.

we had not yet adopted our present view that the triple bond in this molecule is of a $\sigma^2\pi^2\delta^2$ rather than a $\sigma^2\pi^4$ type. As already noted, we now believe that, for the $\sigma^2\pi^4$ type, a shorter distance would be expected, although it is difficult to say how much shorter. Rather than redo the Hartree–Fock calculation at some arbitrarily selected shorter distance, we have turned to the Fenske–Hall method. We first showed that at the same V–V distance, 2.20 Å, it gives results in close agreement with the Hartree–Fock results. We then examined the effect of contracting the V–V distance by extending the Fenske–Hall calculations.

Fenske–Hall Method. Because of its economy and simplicity, the Fenske–Hall method is a very attractive one for use in cases of this sort. There are several published prior examples of its application to compounds with multiple metal–metal bonds[24,25] (as well as the two already discussed in this paper) where it appears to have given reasonable results that were helpful in understanding
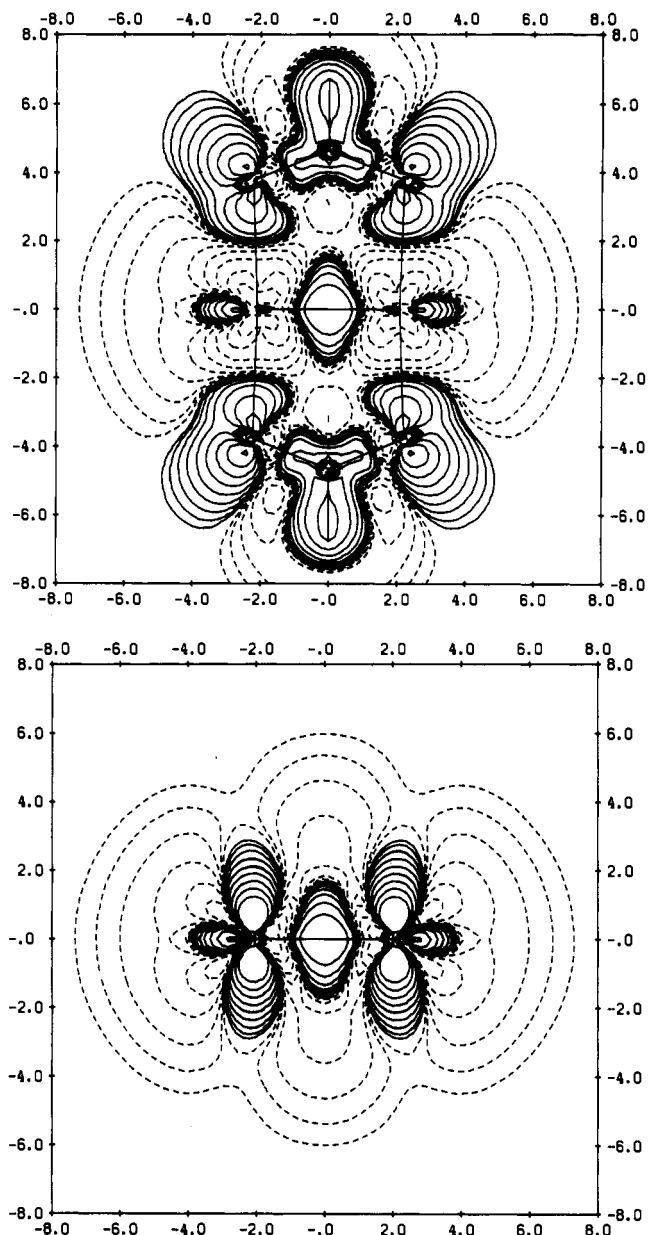
the compounds. However, we know of no case in which there has been a direct comparison between the results of a Fenske–Hall calculation and those of a full-fledged Hartree–Fock calculation on the same system. We have made such a comparison here for the $V_2(O_2CH)_4$ molecule at the V–V distance of 2.20 Å.

In Table IV the orbital energy values calculated by the Fenske–Hall method are listed beside those obtained in the Hartree–Fock calculation. It is evident that the overall agreement is excellent. Although there are small differences in the energies of individual orbitals, the general pattern is qualitatively—and nearly quantitatively—the same in both cases.

With such good agreement between the Hartree–Fock and Fenske–Hall calculations at a V–V distance of 2.20 Å, we felt encouraged in using the latter method to explore the behavior of the $V_2(O_2CH)_4$ molecule as the V–V bond was made shorter. In making these calculations, the dimensions of the formate ions were kept fixed. The results of this study are shown graphically in Figure 8. It can be seen that the energies of the orbitals principally concerned with V–V bonding ($12a_{1g}$, $10e_u$) are not greatly sensitive to the V–V distance over the range (2.2–1.9 Å) in question, although they do show the expected trend toward lower

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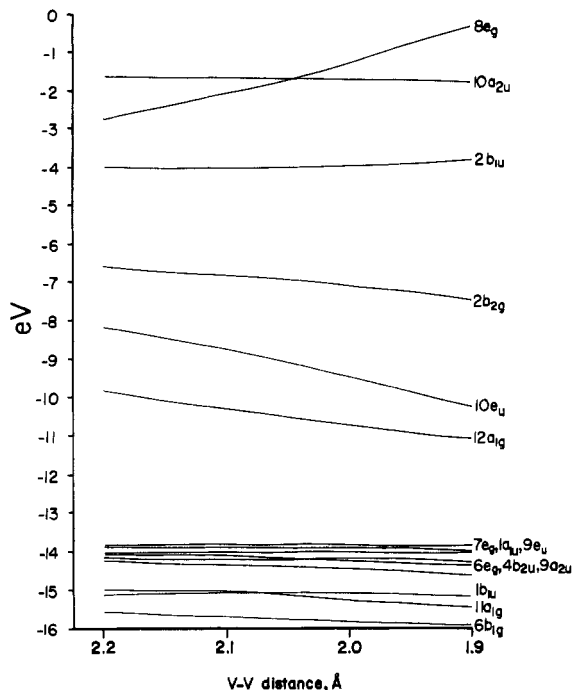
Figure 8. Energies of upper MO's as a function of V–V distance in $V_2(O_2CH)_4$ as calculated by the Fenske–Hall method.

Table IX. Energies (eV) Calculated by the Fenske–Hall Method for $V_2(O_2CH)_4$ at Several V–V Distances

	valence electrons				
V–V, Å	V–V bonds	other	core electrons	core/core interact[a]	total energy
1.9	−31.78	−1655.2	−43 305.1	−1361.5	−46 353.6
2.0	−29.82	−1652.1	−43 298.4	−1376.9	−46 357.2
2.1	−27.90	−1647.6	−43 290.8	−1391.2	−46 357.5
2.2	−26.02	−1643.0	−43 282.7	−1393.3	−46 345.0

[a] Calculated by equation given in: Anderson, A. B. *J. Chem. Phys.* 1975, *62*, 1187 (with suitable adaptation to the point-charge approximation).

values. The total energy of the molecule and of various contributions thereto as a function of internuclear distance are listed in Table IX. These results suggest that the equilibrium configuration of the molecule will have a V–V distance between 2.0 and 2.1 Å. This seems very reasonable when compared to the Cr–Cr distance of 1.96 Å observed[4] in $Cr_2(O_2CCH_3)_4$.

Some Practical Conclusions

This section deals with the following question: On the basis of what has been said above, what sort of compounds containing V–V multiple bonds might the synthetic chemist most prudently attempt to make? We have already noted that for V_2-$(PMePh_2)_4(H_2ZnH_2BH_2)_2$ replacement of the phosphine ligands by two XYZ-type bridging ligands might lead to the stabilization of a quadruple bond between the two V^I (d^4) centers.

The calculations on $V_2(O_2CH)_4$ indicated that $V_2(O_2CR)_4$ molecules should exist in singlet ground states with V≡V bonds.

This does not necessarily mean that preparation of such molecules can confidently be expected. In real laboratory chemistry the important question is whether a given target molecule is stable (thermodynamically or kinetically) relative to other compounds that might be formed from the same components under the same conditions.

We have already had considerable laboratory experience suggesting that while $V_2(O_2CR)_4$ compounds may be accessible by reactions of V^{II}-containing starting materials with RCO_2M reagents, they are probably not the *most stable* products accessible under the reaction conditions. Consequently, they have not been and perhaps cannot actually be isolated. It has been our experience that, instead of $V_2(O_2CR)_4$ molecules, the isolable products of such reactions[26] are the oxo-centered trinuclear species $[V_3(\mu_3$-$O)(O_2CR)_6L_3]^n$ ($n = 0, 1+$). It would appear that vanadium(II) species have a strong tendency to abstract oxygen atoms from carboxyl groups, which leads to their conversion to vanadium(III) species and, ultimately, to the assembly of the V(III)-containing oxo-centered trimers. It is to be noted that even the dichromium species, $Cr_2(O_2CR)_4L_2$, will behave similarly when R and L are chosen (e.g., CHF_2 and pyridine) so as to greatly weaken the Cr—Cr bond.[27] Thus, the reactions of $(NH_4)_4[Cr_2(CO_3)_4(H_2O)_2]$ with CF_2HCO_2H in Et_2O gives initially a purple product, Cr_2-$(O_2CCHF_2)_4(Et_2O)_2$, but when pyridine is diffused into a solution of this compound, the product isolated is $Cr_3(\mu_3$-$O)(O_2CCHF_2)_6(py)_3$.

We have also seen that the 2,6-dimethoxyphenyl ligand, DMP, which is capable of functioning in the desired manner, as a bidentate bridge, e.g., in $Cr_2(DMP)_4$, exercises instead its other capability of functioning as a tridentate ligand in $V_2(DMP)_4$ and thereby gives a structure that is not of the desired type. Again, while the general type of structure (a V_2^{4+} unit bridged by four bidentate three-atom ligands) that we have dealt with in the calculation on $V_2(O_2CH)_4$ may be stable in an absolute sense for $V_2(DMP)_4$, it is *not* stable *relative* to the structure actually adopted.

Clearly, if success is to be achieved in obtaining a triply bonded $V_2(XYZ)_4$ molecule similar to those $Cr_2(XYZ)_4$ species with quadruple bonds formed by chromium, it will be necessary to choose ligands that have the capability to serve as the XYZ ligand but have little or no tendency to do anything else. There are many XYZ ligands other than RCO_2^- and DMP. A synthetic program in which these are systematically tested may well lead to some successful syntheses. The theoretical work reported here is valuable in suggesting that the $V_2(XYZ)_4$ type of compound is not inherently unlikely, but it is the task of the synthetic chemist to discover which XYZ ligand (or ligands) can actually be used.

(26) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3316. Also, unpublished experiments in this Laboratory by Dr. C. A. Murillo.
(27) Cotton, F. A.; Wang, W. *Inorg. Chem.* **1982**, *21*, 2675.