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A Systematic Approach in the Preparation of Compounds with $\sigma^2\pi^4$ Vanadium-to-Vanadium Triple Bonds: Synthesis, Reactivity, and Structural Characterization

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A high-yield synthetic route (90% isolated yield) has been found for the first paddle-wheel divanadium compound with a $\sigma^2\pi^4$ triple bond, $V_2(DFM)_4$ (DFM^- = [(*p*-tolyl)NCHN(*p*-tolyl)]$^-$). The molecule has been characterized by ^{1}H NMR, which shows that it is diamagnetic, with a very large diamagnetic anisotropy, and by X-ray crystallography. It is dimorphous, but the molecules are essentially the same in both forms. In the tetragonal form (space group *P*4/*n*, a = 13.214(6) Å, c = 17.427(5) Å, Z = 2, V = 3043(3) Å^3) V–V = 1.978(2) Å and the torsion angle is 5.4(2)°. In the orthorhombic form (space group *Pccn*, a = 15.555(2) Å, b = 16.914(4) Å, c = 24.768(1) Å, Z = 4, V = 6516(2) Å^3) V–V = 1.975(4) Å and the mean torsion angle is 9.6(6)°. The key step in the synthesis is the use of a THF solution of $VCl_3(THF)_3$ which has been reduced by 1 equiv of $NaHBEt_3$. The compound $V(DFM)_3$ has also been prepared and characterized. It is a tris-chelate compound, strongly distorted from octahedral coordination due to the small bite of the DFM ligands. It forms crystals in space group *C*2/*c* with a = 12.693(4) Å, b = 33.109(6) Å, c = 9.211(3) Å, Z = 4, and V = 3863(2) Å^3.

Introduction

The chemistry and the structural characterization of compounds containing the vanadium(II) ion have slowly been developed in the last few years.[2] Our main motivation was to synthesize and characterize species that would contain a vanadium-to-vanadium triple bond of the type $\sigma^2\pi^4$ with structures similar to those of other transition metal containing species with metal-to-metal multiple bonds.[3] While theoretical calculations had shown that this should be possible,[4] the compounds that had been characterized earlier[5] possessed long V–V bonds (2.20–2.45 Å) and had structures of the edge sharing bioctahedron, ESBO, type.

The earliest attempts were made using the same type of ligands for which other metal–metal-bonded species were known, such as the carboxylato ions, but it was quickly learned that under the reaction conditions that were being used oxidation of vanadium(II) took place, giving instead compounds with a V_3O core.[6]

Later, reactions were carried out using other ligands that were known to form bridges between metal atoms with the hope of either forming the $\sigma^2\pi^4$ vanadium-to-vanadium metal bond or discrediting the idea that the first-row transition elements could form them. When vanadium dichloride complexes containing amine ligands, e.g. $VCl_2(py)_4$ or $VCl_2(TMEDA)_2$, were treated with reagents containing DFM or related anions[5c,7] only mononuclear compounds were isolated. The same was true when other anions having the potential to form bridges, such as $(2\text{-}C_5H_4N)NCH_3^-$ [8] and $o\text{-}C_6H_4CH_2N(CH_3)_2^-$,[9] were employed.

After a systematic study of the chemistry of vanadium(II),[2] it became clear that N-donor molecules formed strong bonds to vanadium(II) and were not, therefore, appropriate as starting materials in the search for compounds with the $\sigma^2\pi^4$ bond. Moreover, attempts to reduce VCl_3 in THF with Zn did not lead to an entirely satisfactory material due to the persistence of zinc in the end products, for example $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn(\mu\text{-}Cl)_2Cl_4]$.[10] Use of this substance as a starting material frequently made isolation of other products difficult and often gave products in which the $[V_2(\mu\text{-}Cl)_3]^+$ core was retained.[11]

The choice of an appropriate ligand was also considered to be crucial. A potentially bridging ligand with only nitrogen atom donor groups was very appealing, but we did not want to arrive at a forced configuration that could raise a question as to the presence of a metal-to-metal bond.

Our first report of a compound for which there was structural evidence of the presence of a triple V–V bond with a paddle-wheel arrangement of the ligands about the divanadium unit appeared recently.[12] Two different types of crystals were reported to be isolable from the reaction of solutions of vanadium(II) chloride and lithium *N*,*N'*-di-*p*-tolylformamidinate, LiDFM, in THF. Only for one of these compounds had it been possible to obtain crystallographic data up to the time of our preliminary note.[12] We now report the chemical characterization of both of these solids, the complete structural results from the tetragonal crystals, important structural results from the orthorhombic crystals, and the reactivity of the compound toward a strong base such as pyridine, as well as the structural characterization of tris(*N*,*N'*-di-*p*-tolylformamidinato)vanadium(III).

Experimental Section

All manipulations were carried out under argon using standard Schlenk techniques. The solvents were purified by conventional methods and were freshly distilled under nitrogen prior to use. $VCl_3(THF)_3$ was

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(2) See, for example: Cotton, F. A.; Daniels, L. M.; Montero, M. L.; Murillo, C. A. *Polyhedron* **1992**, *11*, 2767 and references cited therein.

(3) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, England, 1993.

(4) Cotton, F. A.; Diebold, M. P.; Shim, I. *Inorg. Chem.* **1985**, *24*, 1510.

(5) (a) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7866. (b) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 560. (c) Edema, J. J. H.; Meetsma, A.; van Bolhuis, F.; Gambarotta, S. *Inorg. Chem.* **1991**, *30*, 2056.

(6) Cotton, F. A.; Extine, M. W.; Falvello, L. R.; Lewis, D. B.; Lewis, G. E.; Murillo, C. A.; Schwotzer, W.; Tomas, M. *Inorg. Chem.* **1986**, *25*, 3505.

(7) Cotton, F. A.; Poli, R. *Inorg. Chim. Acta* **1988**, *141*, 91.

(8) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Spek, A. L.; Veldman, N. *Inorg. Chem.* **1991**, *30*, 2062.

(9) Edema, J. J. H.; Stauthamer, W.; van Bolhuis, F.; Gambarotta, S.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1990**, *29*, 1302.

(10) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 913.

(11) Cotton, F. A.; Duraj, S. A.; Roth, W. J.; Schmulbach, C. D. *Inorg. Chem.* **1985**, *24*, 525.

(12) Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 737.

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Table I. Crystallographic Data

	$V_2(DFM)_4$·toluene (tetragonal form)	$V(DFM)_3$
formula	$V_2N_8C_{67}H_{68}$	$VN_6C_{45}H_{45}$
fw	1087.2	720.84
space group	*P*4/*n*	*C*2/*c*
a, Å	13.214(6)	12.693(4)
b, Å		33.109(6)
c, Å	17.427(5)	9.211(3)
β, deg		93.74(2)
V, Å^3	3043(3)	3863(2)
Z	2	4
d_{calcd}, g/cm^3	1.19	1.24
μ, cm^{-1}	29.36 (Cu Kα)	2.851 (Mo Kα)
λ, Å	1.541 84	0.710 73
T, °C	22(1)	–75(1)
transm factors: max, min	1.0000, 0.9285	0.9999, 0.9220
R^a	0.049	0.050
$R_w{}^b$	0.068	0.068

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Positional Parameters and Their Estimated Standard Deviations for the Metal Complex Atoms of $V_2(DFM)_4$·toluene[a]

atom	*x*	*y*	*z*	*B*, Å^2
V(1)	0.250	0.250	0.17642(8)	4.06(2)
V(2)	0.250	0.250	0.06290(8)	3.92(2)
N(1)	0.3000(3)	0.1004(3)	0.1855(2)	4.72(4)
N(2)	0.2864(3)	0.0942(3)	0.0540(2)	4.60(4)
C(1)	0.3079(3)	0.0517(3)	0.1207(3)	4.88(4)
C(2)	0.3296(4)	0.0462(3)	0.2526(3)	5.05(4)
C(9)	0.2977(3)	0.0356(3)	–0.0137(2)	4.63(4)
C(3)	0.4182(4)	–0.0092(4)	0.2544(3)	6.92(4)
C(4)	0.4457(5)	–0.0596(5)	0.3206(3)	9.22(4)
C(5)	0.3874(5)	–0.0563(5)	0.3853(3)	8.41(4)
C(6)	0.3007(5)	0.0013(5)	0.3828(3)	7.93(4)
C(7)	0.2729(4)	0.0526(4)	0.3180(3)	6.40(4)
C(8)	0.4140(6)	–0.1184(6)	0.4572(4)	13.53(4)
C(10)	0.2343(4)	0.0526(4)	–0.0744(3)	6.65(4)
C(11)	0.2467(5)	–0.0011(5)	–0.1427(3)	7.94(4)
C(12)	0.3209(5)	–0.0710(4)	–0.1522(3)	7.05(4)
C(13)	0.3788(6)	–0.0887(5)	–0.0910(3)	10.92(4)
C(14)	0.3700(5)	–0.0349(5)	–0.0227(3)	8.92(4)
C(15)	0.3330(6)	–0.1277(5)	–0.2282(3)	10.54(4)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3(a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for the Tetragonal Form of $V_2(DFM)_4$[a]

V(1)–V(2)	1.978(2)	N(1)–C(2)	1.426(6)
V(1)–N(1)	2.091(4)	N(2)–C(1)	1.321(6)
V(2)–N(2)	2.120(4)	N(2)–C(9)	1.419(6)
N(1)–C(1)	1.305(6)		
V(2)–V(1)–N(1)	94.4(1)	V(1)–N(1)–C(2)	128.6(3)
N(1)–V(1)–N(1′)	89.7(1)	C(1)–N(1)–C(2)	116.2(4)
N(1)–V(1)–N(1″)	171.3(2)	V(2)–N(2)–C(1)	113.4(3)
V(1)–V(2)–N(2)	94.2(1)	V(2)–N(2)–C(9)	127.9(3)
N(2)–V(2)–N(2′)	89.7(1)	C(1)–N(2)–C(9)	118.5(4)
N(2)–V(2)–N(2″)	171.6(2)	N(1)–C(1)–N(2)	122.4(4)
V(1)–N(1)–C(1)	115.2(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

prepared as reported.[13] The preparation of $V_2(DFM)_4$ and both the tetragonal (T-form) and orthorhombic (O-form) crystals of it has been described in detail in our earlier report.[12] The IR spectra were recorded on a Perkin-Elmer 783 spectrometer. UV-vis spectra were obtained on a Cary 17D spectrometer. Magnetic measurements were performed on a Johnson-Matthey MSB-1 balance.

$V(DFM)_3$. $VCl_3(THF)_3$ (0.20g, 0.53 mmol) was dissolved in 10 mL of THF, and the solution was cooled to –70 °C. To this was added a cold suspension of LiDFM (1.6 mmol) in 10 mL of THF. After mixing, the reaction mixture was reddish-violet and it was then allowed to return to room temperature. After 90 min the solvent was removed under vacuum. To the solid that remained was added 20 mL of warm toluene, and the mixture was filtered. Only a colorless solid remained on the filter frit (LiCl). To the solution was added a layer of 20 mL of hexanes, and the mixture was cooled to –10 °C for 3 days. Dark reddish-violet crystals were isolated by filtration and washed with small amounts of hexanes (0.19 g, 51% yield). Further crops of crystals were obtained by taking the filtrate to dryness and repeating the extraction cycle with smaller amounts of toluene. IR (cm^{-1}): 1655 (w), 1600 (w), 1498 (s), 1302 (w), 1270 (m), 1252 (s), 1162 (w), 1150 (w), 954 (s), 820 (m), 804 (s). UV–vis (toluene): λ_{max} 542 nm (ϵ 1.7 × 10^3). Magnetic moment: 2.72 μ_B.

Crystallographic Studies

Data Collection and Reduction. Both the T-form and O-form crystals of $V_2(DFM)_4$ were attached to the tips of glass fibers for room-temperature study on a Rigaku AFC5R diffractometer. The crystal of $V(DFM)_3$ was studied on a CAD-4 diffractometer at –75 °C. The procedures used for data collection have been described previously.[14] In each case, the Laue group and lattice repeats were confirmed via axial photography, and azimuthal scans (ψ-scans) were used as the basis of an empirical absorption correction. Monitor reflections indicated a 14.4% decay in the T-form crystal of $V_2(DFM)_4$ and a 18.6% decay in the O-form crystal. The $V(DFM)_3$ crystal suffered no loss in intensities.

Structure Solution and Refinement. Initial positions for the T-form of $V_2(DFM)_4$ were taken from the isotypic structure of $W_2(DFM)_4$·C_7H_8. The details of the refinement and the handling of the disordered toluene molecule were described in our earlier report[12] Table I contains other data pertinent to the data collection and structure refinement. Positional parameters are listed in Table II, and important bond distances and angles, in Table III.

Since the crystals of the O-form of $V_2(DFM)_4$ were consistently small and somewhat weakly diffracting, a large number of data were unobserved ($F_o{}^2 < 3\sigma(F_o{}^2)$). Since the structure is isotypic with that of $Ru_2(DFM)_4$·C_6H_6, the starting positions of the metal complex atoms from the ruthenium structure were used.[15] The atoms of the metal complex refined smoothly, but no distinct solvent molecule could be modeled from the significant peaks in the resulting difference maps. A model for the solvent that contained 12 separate carbon atoms with occupancy factors of about 0.5 would refine and serve to reduce the residuals, but no sensible molecule could be deduced from the arrangement. No further refinement was attempted since the geometry of the metal complex was well-defined and matched the chemical characterization data.[16] Both of the $V_2(DFM)_4$ structures were refined using the SHELX-76 program.

The initial positions of the non-hydrogen atoms of the $V(DFM)_3$ structure were taken from a direct-methods *E* map. The metal atom and one of the bridgehead carbon atoms (atom C(16)) of the chelating DFM groups reside on a crystallographic 2-fold axis, so that two complete chelating ligands are related by symmetry, and the third ligand has 2-fold symmetry itself. However, disorder in the ligand on the 2-fold axis was evident even from the direct-methods results. The planes describing the two orientations of the disordered tolyl rings form an angle of about 60° to each other and form a line of intersection approximately along the bond between atoms C(18) and C(19). The positions of these two atoms are shared by both orientations of the disordered rings (or, more likely, the positions are so close to one another as to be indistinguishable). Refinement of the relative occupancies of the two orientations always resulted in a value equal to 50% within its standard deviation, so the value was fixed for the final refinement cycles. An examination of the intermolecular contacts revealed that, for any given complete complex, the two orientations of the disordered *p*-tolyl groups must be different in order to avoid impossible contacts. This means that the two orientations must alternate from one equivalent position to the next. This could conceivably lead to long-range order indicated by a larger cell, or a

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(13) Manzer, L. *Inorg. Synth.* **1982**, *21*, 135.

(14) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(15) Cotton, F. A.; Ren, T. *Inorg. Chem.* **1991**, *30*, 3675.

(16) The O-type crystals of $V_2(DMF)_4$ form in space group *Pccn* with cell parameters *a* = 15.555(2) Å, *b* = 16.914(4) Å, *c* = 24.768(1) Å, *V* = 6516(3) Å^3, and *Z* = 4. Out of 4849 unique data, 1564 having $F_o{}^2 \geq 3\sigma(F_o{}^2)$ were used to refine 201 parameters resulting in residuals of *R* = 0.093 and R_w = 0.112 and quality-of-fit = 2.02. Important bond distances (Å): V(1)–V(2), 1.974(4); V(1)–N(1), 2.11(1); V(1)–N(2), 2.09(1); V(2)–N(3), 2.10(1); V(2)–N(4), 2.08(1). Additional data are available as supplementary material.

Table IV. Positional Parameters and Their Estimated Standard Deviations for $V(DFM)_3$[a]

atom	*x*	*y*	*z*	*B*, Å^2
V	0.000	0.11514(3)	0.250	2.69(2)
N(1)	0.0290(2)	0.0768(1)	0.0822(4)	2.76(7)
N(2)	−0.1284(3)	0.1034(1)	0.1013(3)	2.81(7)
N(3)	0.0413(3)	0.1687(1)	0.1487(3)	2.97(7)
C(1)	−0.0688(3)	0.0813(1)	0.0227(4)	2.77(8)
C(2)	0.1109(3)	0.0574(1)	0.0148(4)	2.77(8)
C(3)	0.0934(3)	0.0272(1)	−0.0904(4)	2.99(9)
C(4)	0.1798(3)	0.0090(1)	−0.1485(5)	3.51(9)
C(5)	0.2827(3)	0.0200(1)	−0.1087(5)	3.6(1)
C(6)	0.2974(3)	0.0497(2)	−0.0044(5)	4.0(1)
C(7)	0.2135(3)	0.0680(1)	0.0567(5)	3.44(9)
C(8)	0.3756(4)	0.0001(2)	−0.1736(6)	5.2(1)
C(9)	−0.2349(3)	0.1133(1)	0.0631(4)	2.63(8)
C(10)	−0.2982(4)	0.0928(1)	−0.0403(5)	4.0(1)
C(11)	−0.4013(4)	0.1049(2)	−0.0695(5)	4.6(1)
C(12)	−0.4443(4)	0.1373(1)	−0.0009(5)	4.2(1)
C(13)	−0.3806(4)	0.1570(1)	0.1043(5)	4.0(1)
C(14)	−0.2779(3)	0.1453(1)	0.1345(5)	3.49(9)
C(15)	−0.5590(4)	0.1504(2)	−0.0363(7)	6.3(1)
C(16)	0.000	0.1909(2)	0.250	3.0(1)
C(17)	0.0573(6)	0.1838(2)	0.0087(8)	2.4(2)
C(18)	0.1238(4)	0.1640(1)	−0.0774(5)	3.37(9)
C(19)	0.1663(4)	0.1787(1)	−0.1977(5)	4.2(1)
C(20)	0.1144(7)	0.2131(3)	−0.2609(9)	3.2(2)
C(21)	0.0410(7)	0.2337(2)	−0.1817(9)	3.6(2)
C(22)	0.0140(7)	0.2186(2)	−0.0480(9)	3.2(2)
C(23)	0.1417(8)	0.2298(3)	−0.405(1)	4.7(2)
C(17A)	0.1087(6)	0.1869(3)	0.0457(9)	3.0(2)
C(20A)	0.2250(7)	0.2171(3)	−0.1769(9)	3.3(2)
C(21A)	0.2157(7)	0.2386(3)	−0.050(1)	3.7(2)
C(22A)	0.1574(7)	0.2244(3)	0.0590(9)	3.5(2)
C(23A)	0.2902(8)	0.2329(3)	−0.299(1)	5.1(2)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

Table V. Selected Distances (Å) and Angles (deg) for $V(DFM)_3$

V–N(1)	2.053(3)	V–N(3)	2.087(3)
V–N(2)	2.096(3)		
N(1)–V–N(1′)	103.5(1)	N(2)–V–N(2′)	158.5(1)
N(1)–V–N(2)	64.1(1)	N(2)–V–N(3)	94.2(1)
N(1)–V–N(2′)	101.9(1)	N(2)–V–N(3′)	104.1(1)
N(1)–V–N(3)	97.3(1)	N(3)–V–N(3′)	63.6(1)
N(1)–V–N(3′)	157.7(1)		

superlattice. However, the axial photographs did not reveal this condition, possibly because of the limited diffracting power of the crystals. Intensity statistics suggested that the centrosymmetric space group *C*2/*c* was indeed the correct choice. However, *Cc* was tried in an attempt to remove the need for disorder in the model, but the disorder persisted.

In the final stages of refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were used in idealized positions, 0.95 Å from the attached carbon atoms, for the calculation of structure factors. Table I contains additional crystallographic data. Positional parameters are given in Table IV. The more important distances and angles are given in Table V. Refinement was carried out using the SDPVAX programs.

Results and Discussion

Method of Synthesis. Isolated yields of $V_2(DFM)_4$ can be as high as 90%, and we believe that the reaction is essentially quantitative. As indicated in our earlier report,[12] the reaction of a solution of vanadium(II) chloride in THF and LiDFM affords two different types of crystals of $V_2(DFM)_4$ upon extraction with toluene. Both of these, when dissolved in benzene, gave the same NMR spectrum. The long and thin copper-colored O-form crystals are obtained exclusively by taking the first extraction of the dried reaction mixture with toluene and cooling to −70 °C. The yield of crystalline product, isolated in this way, was 52%. However, if after filtration, the mother liquor is taken to dryness, an amorphous product is obtained that gives the same sharp NMR spectrum, and when this is added to the previous material, the total yield reaches *ca.* 90%. A layer of hexanes added to the original solution followed by cooling to −70 °C produces the T-form crystals in higher yield.

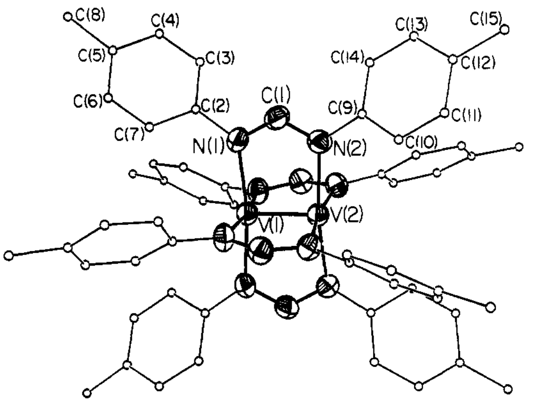

Figure 1. ORTEP drawing of the tetragonal form of $V_2(DFM)_4$. The core atoms are represented by their 40% probability ellipsoids, and the atoms of the tolyl groups are drawn as arbitrarily-sized spheres.

The "$VCl_2(THF)_n$" solution, generated by reduction of $VCl_3(THF)_3$ with $NaHBEt_3$, is important in the success of this synthesis. Other reducing agents, such as Na/Hg, produced different products.

The T-form crystals, red-violet and blocked-shaped, were obtained exclusively by dissolving the O-form crystals in toluene and then layering the solution with hexanes and allowing it to remain at room temperature.

Comparison of the T- and O-form Structures. A 4-fold axis along the metal-to-metal vector in the T-form structure requires the equivalence of all the DFM ligands. The vanadium-to-vanadium bond length of 1.978(2) Å is the second shortest of any of the $M_2(DFM)_4$ compounds known, only that for the chromium analog (1.930(2) Å)[17] being shorter. Indeed, as noted earlier,[12] the "formal shortness ratio" (FSR) of this V≡V bond, a measure of bond shortness normalized to intrinsic atomic size, is only 0.808. This is even smaller than the FSRs for many quadruple bonds, such as those in the group VI $M_2(DFM)_4$ series: 0.814 (Cr), 0.840 (Mo), 0.838 (W).

As indicated under Crystallographic Studies, the O-form crystals were of marginal quality; they grew very long and very thin, being almost hairlike. However, since they gave the same NMR spectrum as the T-form and crystallized in the same space group as $Ru_2(DFM)_4{\cdot}C_6H_6$[15] with atomic coordinates for the dinuclear unit that correspond closely to those of the ruthenium compound, we are confident of our results. The vanadium atoms in the O-form reside on a crystallographic 2-fold axis. The distance between vanadium atoms is 1.974(4) Å, which is indistinguishable from that in the T-form.

The only appreciable difference between the molecules in the two forms is a small change in the twist angles of the ligands around the metal centers. While the torsion angle of the T-form is 5.4(2)°, the mean torsion angle for the O-form is 9.6(6)°. Figure 1 is a drawing of the structure of the T-form but is generally representative of the O-form.

Reactivity. The $V_2(DFM)_4$ molecule is very stable in THF, toluene, and benzene solutions as long as they are protected from oxygen. In the presence of dry oxygen, they react to produce reddish orange $V_2O_2(DFM)_4$ and the corresponding greenish monomer $VO(DFM)_2$. These results will be discussed in more detail elsewhere,[18] since these two products are themselves interesting.

In pyridine solution, the dinuclear $V_2(DFM)_4$ species is stable for short periods of time. An analysis of the NMR spectra of the

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(17) Cotton, F. A.; Ren, T. *J. Am. Chem. Soc.* **1992**, *114*, 2237.

(18) Cotton, F. A.; Murillo, C. A. Unpublished results.

solid that remains after the pyridine solutions are dried shows that the dinuclear unit remains intact after 1 h at room temperature. However, if the solutions are refluxed in neat pyridine, the color rapidly changes to produce the mononuclear compound *trans*-V(py)$_2$(DFM)$_2$, as determined by comparison of the unit cell of the crystalline product and its IR spectrum to those published previously.[7] This type of bridge cleavage by pyridine has been observed previously in other compounds that contain a metal-to-metal bond.[19,20]

Other Considerations. One important question that might be asked is whether the DFM ligand forces the formation of the dinuclear unit. Compounds containing the bridging DFM ligand or very similar ones that have metal-to-metal bonds are known for Ti,[21] Cr,[17] Mo,[22] W,[17] Re,[23] Ru,[15,24] Os,[25] Co,[26] Rh,[27] Ir,[28] and Pt.[29] Also known are compounds that contain bridging DFM ligands between metal atoms that do not possess such a bond, examples being the M$_2$(DFM)$_4$ compounds of nickel and palladium[30] and M$_2$(DFM)$_4$ compounds of copper and silver.[31] In general, metal-to-metal distances range from 1.930 Å for chromium to 2.705 Å for the silver compound.

It is noteworthy that the angle formed by the metal center, the nitrogen atom, and the carbon atom of the methine group of the DFM ligand varies significantly for the different types of dinuclear compounds. It is nearly 120° for those cases in which there is no metal-to-metal bond but smaller for those in which a strong metal-to-metal bond is present. In the T-form of V$_2$(DFM)$_4$ those angles are only 115.2(3) and 113.9(3)°.

The DFM ligand also forms chelate complexes as in the compounds Ti$_2$(RNC(H)NR)$_2$(μ-RNC(H)NR)$_2$(μ-Cl)$_2$,[21] V(DFM)$_3$ (vide infra), *trans*-V(py)$_2$(DFM)$_2$,[7] and (PhNCHNPh)$_2$V(TMEDA).[5c] The latter two compounds were prepared from the reaction of VCl$_2$(py)$_4$ and VCl$_2$(TMEDA)$_2$, respectively, and the corresponding lithium formamidinate. To prepare the V$_2$(DFM)$_4$ species, we used a similar route but the oxygen-donor ligand THF instead of the nitrogen-donor py or TMEDA.

The appearance of the tris-chelate complex V(DFM)$_3$ is also indicative of the flexibility of the DFM ligand. In this compound, the oxidation state of the vanadium atom is higher and consequently the vanadium radius is smaller than in the case of the vanadium(II) species. From steric considerations, one would expect the formation of the tris-chelate to be more difficult for vanadium(III) than for vanadium(II).

Recently, still another bonding mode was reported for a closely related ligand, the triazene analog. In the compound Rh$_2$(μ-CO)(bipy)(dppe)(μ-RNNNR-$N^{1,3}$,N^3)(μ-RNNNR-N^1,N^3)(PF$_6$)$_2$, one of the triazene groups bridges the two metal atoms in the usual way, with one metal-to-nitrogen bond to each metal atom, while in the other group one of the nitrogen atoms binds to two metal centers simultaneously.[32]

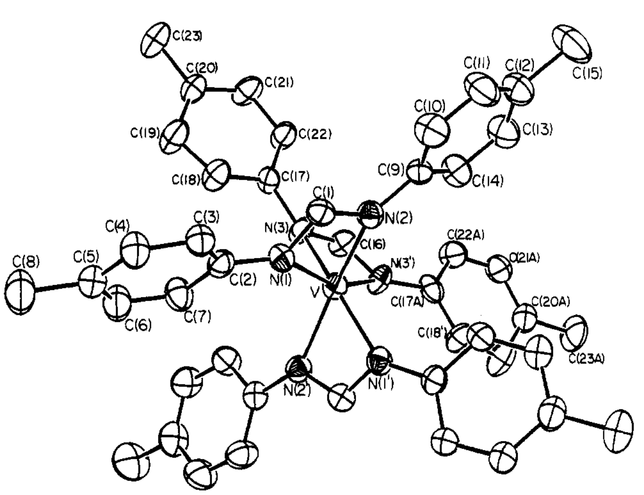

Figure 2. ORTEP drawing of the molecular structure of V(DFM)$_3$ showing the atom-labeling scheme. Atoms are represented by their 50% probability ellipsoids.

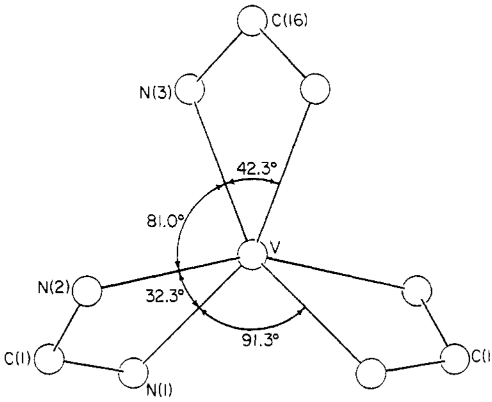

Figure 3. Bonds of the coordination sphere of V(DFM)$_3$ projected onto the plane defined by atoms C(1), C(1′), and C(16). Atoms V and C(16) lie on a crystallographic 2-fold axis.

In view of its extremely varied behavior, we do not believe that the DFM ligand is forcing a close vanadium-to-vanadium contact, but simply supporting it. That there is, indeed, a V≡V bond is indicated by the very short intermetallic distance (*ca.* 1.978 Å) and the very high magnetic anisotropy displayed by the molecule, namely 7300 × 10^{-36} m^3 molecule^{-1}.[12]

Mononuclear V(DFM)$_3$. This compound forms in essentially quantitative yield from the reaction of VCl$_3$(THF)$_3$ with LiDFM. An ORTEP drawing of the molecule is shown in Figure 2. The conformation of the atoms directly bound to the vanadium atom is that of a highly distorted octahedron. This condition is imposed by the formation of highly strained N–V–N bonds with angles in the range 63.6–64.1°, which are somewhat similar to those found in analogous compounds, namely tris(1,3-diphenyltriazenato)cobalt(III)[33] and -chromium.[34] Because of this strain resulting from the small bite of the DFM ligand, the configuration of the six coordinated nitrogen atoms about the vanadium(III) atom is markedly distorted from trigonal antiprismatic toward prismatic. This is shown in Figure 3. The two sets of angles formed by projection of the structure down the idealized 3-fold

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(19) Alfaro, N. M.; Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Inorg. Chem.* **1992**, *31*, 2718.

(20) Lindsay, A. J.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 2723.

(21) Cotton, F. A.; Wojtczak, W. A. *Gazz Chim. Ital.*, in press.

(22) Cotton, F. A.; Feng, X.; Matusz, M. *Inorg. Chem.* **1989**, *28*, 594.

(23) Cotton, F. A.; Ren, T. *J. Am. Chem. Soc.* **1992**, *114*, 2495.

(24) (a) Cotton, F. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 5761. (b) Cotton, F. A.; Falvello, L. R.; Ren, T.; Vidyasagar, K. *Inorg. Chim. Acta* **1992**, *194*, 163. (c) Bear, J. L.; Han, B.; Huang, S. *J. Am. Chem. Soc.* **1993**, *115*, 1175.

(25) Cotton, F. A.; Ren, T.; Eglin, J. L. *Inorg. Chem.* **1991**, *30*, 2559.

(26) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1987**, *26*, 3652.

(27) (a) Bruno, G.; Schiavo, S. L.; Tresoldi, G.; Piraino, P.; Valli, L. *Inorg. Chim. Acta* **1992**, *196*, 131. (b) Piraino, P.; Bruno, G.; Schiavo, S. L.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 2205. (c) Piraino, P.; Bruno, G.; Nicolò, F.; Faraone, F.; Schiavo, S. L. *Inorg. Chem.* **1985**, *24*, 4760. (d) Bear, J. L.; Yao, C.-L.; Lifsey, R. S.; Korp, J. D.; Kadish, K. M. *Inorg. Chem.* **1991**, *30*, 336. (e) Bruno, G.; Tresoldi, G.; Schiavo, S. L.; Sergi, S.; Piraino, P. *Inorg. Chim. Acta* **1992**, *197*, 9.

(28) (a) Cotton, F. A.; Poli, R. *Polyhedron* **1987**, *6*, 1625. (b) Cotton, F. A.; Poli, R. *Inorg. Chim. Acta* **1986**, *122*, 243.

(29) Cotton, F. A.; Matonic, J. H. Unpublished results.

(30) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144.

(31) Cotton, F. A.; Feng, X.; Matusz, M.; Poli, R. *J. Am. Chem. Soc.* **1988**, *110*, 7077.

(32) Connelly, N. G.; Hopkins, P. M.; Orpen, A. G.; Rosair, G. M.; Viguri, F. *J. Chem. Soc., Dalton Trans.* **1992**, 2907.

(33) (a) Krigbaum, W. R.; Rubin, B. *Acta Crystallogr.* **1973**, *B29*, 749. (b) Corbett, M.; Hoskins, B. F. *Aust. J. Chem.* **1974**, *24*, 665.

(34) Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1143.

axis have average values of 35.6 and 84.4° instead of their all being 60° as in a true trigonal antiprism.[35]

Concluding Remarks. The long search for a synthetic procedure for the elusive vanadium-to-vanadium triple bond has now reached a successful conclusion with the preparation and structural characterization of the two different forms of tetrakis(*N*,*N'*-di-*p*-tolylformamidinato)divanadium(II). A short metal-to-metal separation, a small "formal shortness ratio", the complete diamagnetism, and the high magnetic anisotropy all point to a very strong bond. In addition, in the course of these studies, much useful knowledge has been gained about the chemical behavior of V^{II}, which, until a few years ago, was very poorly understood.

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Supplementary Material Available: Tables of crystallographic data, positional parameters, complete bond distances and angles, and anisotropic displacement parameters for $V(DFM)_3$ and both forms of $V_2(DFM)_4$, tables of calculated hydrogen positions for $V(DFM)_3$ and $V_2(DFM)_4$ (T-form), and an ORTEP drawing of $V_2(DFM)_4$ (O-form) (24 pages). Ordering information is given on any current masthead page.

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(35) We are in the process of writing a paper describing in detail the syntheses and characterization of a series of $M(formamidinate)_3$ and $M(triazinate)_3$ complexes. Further discussion of this type of structure will be given there.