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Synthesis and Structure of a Trigonal Monopyramidal Vanadium(III) Complex, $[(C_6F_5NCH_2CH_2)_3N]V$, and the Vanadium(IV) Product of Its Oxidation, $\{[(C_6F_5NCH_2CH_2)_2N(CH_2CH_2NHC_6F_5)]V(O)\}_2$

Celine Rosenberger, Richard R. Schrock,* and William M. Davis

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Introduction

A vanadium triamidoamine complex such as d^2 $[(RNCH_2CH_2)_3N]V$ (e.g., R = trialkylsilyl) would seem likely to form a bimetallic or a monomeric dinitrogen complex for several reasons. First, the apical coordination site contains two orthogonal π orbitals and a σ orbital pointing along the z axis, a circumstance that is optimal for binding dinitrogen in an "end-on" fashion.[1] Second, two triamidoamine complexes of molybdenum are known that contain a bridging dinitrogen, $\{[N_3N_F]Mo\}_2(N_2)$[2] ($[N_3N_F]^{3-}$ = $[(C_6F_5NCH_2CH_2)_3N]^{3-}$) and $\{[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]Mo\}_2(N_2)$.[3] Third, monometallic triamidoamine complexes that contain a single dinitrogen are known, the sodium salt of the d^4 "Mo(II)" species, $\{[N_3N_F]Mo(N_2)\}^-$,[2] and the isoelectronic Re(III) species, $[N_3N_F]Re(N_2)$.[4] Fourth, a wide variety of vanadium triamidoamine complexes have been reported that contain a bulky silyl group[5−10] or the $[N_3N_F]^{3-}$ ligand.[11] Finally, among the variety of recently prepared vanadium complexes that contain dinitrogen[12−20] are V(III) complexes that contain a μ dinitrogen ligand. However, the d^3 "trigonal monopyramidal" complex, $[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]V$,[7] does not form either a terminal or a μ dinitrogen complex readily. Here we show that $[N_3N_F]V$, which can be prepared by reduction of $[N_3N_F]VCl$ in a noncoordinating solvent, also does not bind dinitrogen, or even carbon monoxide.

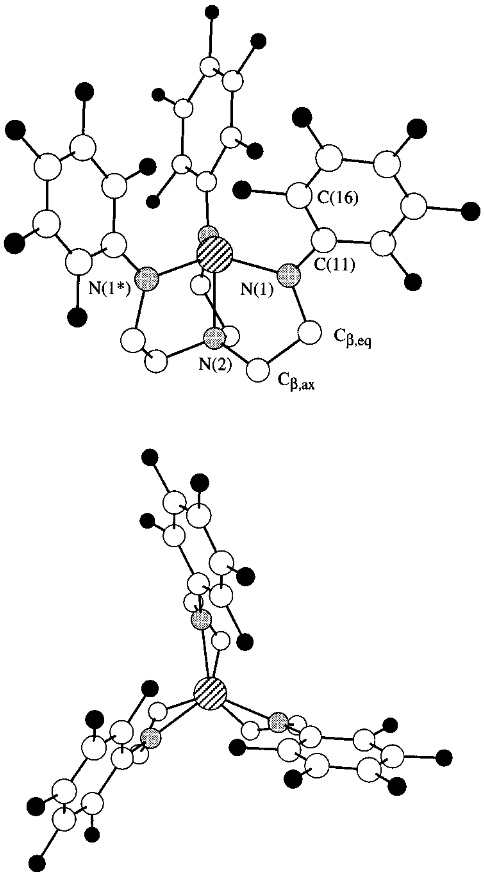
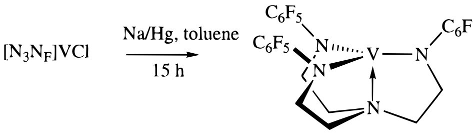


Figure 1. Two views of $[(C_6F_5NCH_2CH_2)_3N]V$.

Results and Discussion

Reduction of $[N_3N_F]VCl$[11] with sodium amalgam in THF is known to yield $[N_3N_F]V(THF)$, in which THF occupies the apical coordination position in an approximate trigonal bipyramid. Other σ-bonding ligands such as nitriles or chloride ion will form related species. However, reduction of $[N_3N_F]VCl$ with sodium amalgam in toluene yields dark green paramagnetic $[N_3N_F]V$ (**1**, eq 1) instead of the sodium salt of known[11] $\{[N_3N_F]VCl\}^-$. The observed magnetic moment of $[N_3N_F]V$ at room temperature by the Evans method was 3.7 μ_B, slightly higher than μ for $[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]V$[7] (3.1 μ_B), but essentially the same as that for $[N_3N_F]V(THF)$ (3.7 μ_B).[11] All data are consistent with these complexes being high-spin V(III) (d^3) species.



(1)

The crystal structure of **1** (Figure 1) shows it to be a trigonal monopyramid with a core structure that is closely similar to that of $[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]V$[7] (Table 1). The vanadium atom is displaced from the amido plane by only 0.21 Å in the direction of the vacant coordination site, and the V−N(2) bond length is consequently relatively short. The V−N(1)−C(11) angle is approximately 125°, a typical value for many triamidoamine complexes.[1] Since $C_{\beta,ax}$ is the "flap" in the envelope-shaped VN_2C_2 ring, the N(2)−V−N(1)−C(11) dihedral angle is close to 180°. An important difference between the structure

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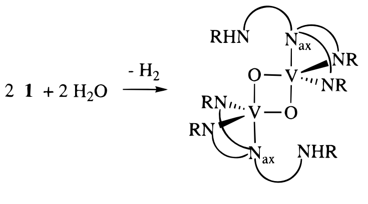
Table 1. Summary of Crystallographic Data for **1** and **2**

	1	**2**
empirical formula	$C_{24}H_{12}F_{15}N_4V$	$C_{24}H_{13}F_{15}N_4VO$
fw	692.32	709.31
a (Å)	14.40(2)	24.4401(4)
b (Å)	14.40(2)	19.2403(4)
c (Å)	21.84(4)	17.0602(2)
α (deg)	90	90
β (deg)	90	116.3690(10)
γ (deg)	120	120
V (Å^3)	3923(9)	7187.6(2)
space group	$R\bar{3}$	*C*2/*c*
Z	6	8
ρ_{Calcd} (g cm^{-3})	1.758	1.309
R_1 (all data)[a]	0.0697	0.0801

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

of **1** and an analogous $[N_3N_F]^{3-}$ complex that contains a ligand in the apical coordination site (such as $[N_3N_F]V(THF)$[11] or $[N_3N_F]MoCl$[2]) is that the three C_6F_5 rings are not arranged to produce a bowl-like cavity, but turned so that the ortho fluorines “fill” the apical cavity. In fact, the $V\cdots F_{\mathrm{ortho}}$ distance (2.652 Å) could be construed as a weak interaction. The positions of the fluorines are roughly the same relative to the $V(N_{eq})_3$ framework as the three hydrides in $[(Me_3SiNCH_2CH_2)_3N]WH_3$.[21] It is still possible that the C_6F_5 rings are oriented the way they are only for steric reasons and that the $V\cdots F_{\mathrm{ortho}}$ distance is circumstantially short.

Compound **1** reacts readily with THF to give $[N_3N_F]V(THF)$, and like $[N_3N_F]V(THF)$, it reacts with propylene oxide to afford $[N_3N_F]V{=}O$.[11] However, it does not react with CO at 1 atm and room temperature over a period of 24 h. Not surprisingly, therefore, it also does not form stable $[N_3N_F]V(N_2)$. Apparently, a good *σ*-donating ligand will bind to $[N_3N_F]V$ to form an adduct in which the electronic configuration can remain high spin. Ligands that would bind largely via *π* back-bonding do not bind to $[N_3N_F]V$, perhaps largely because the low-spin configuration in triamidoamine complexes of this sort is required for efficient binding and the high energy of the low-spin configuration cannot be compensated by a high metal−ligand bond strength. Somewhat surprisingly, however, there also is no indication that **1** will form a *μ* dinitrogen complex analogous to several known V(III) complexes and related to the Mo(IV) “diazenido(2−)” species, $[N_3N_F]Mo{-}N{=}N{-}Mo[N_3N_F]$.[2]



(2)

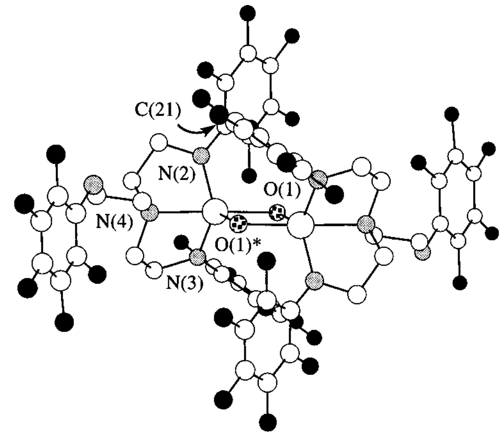


Figure 2. A view of the structure of $\{[(C_6F_5NCH_2CH_2)_2N(CH_2CH_2NHC_6F_5)]V(O)\}_2$.

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for $[(RNCH_2CH_2)_3N]V$ (R = C_6F_5 or *t*-$BuMe_2Si$[a])

	C_6F_5	*t*-$BuMe_2Si$
V−N(1)	1.947(4)	1.926(13)
V(1)−N(2)	2.079(6)	2.083(3)
V−N(1)−X	125.4(3) (X = C(11))	127.6(2) (X = Si)
N(1)−V−N(1*)	118.72(4)	119.2(1)
N(2)−V(1)−N(1)	83.45(10)	84.9(1)

[a] See ref 7.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for $\{[(C_6F_5NHCH_2CH_2)(C_6F_5NCH_2CH_2)_2N]VO\}_2$

V−O(1)	2.042(4)	V−N(3)	1.909(5)
V−O(1)*	1.953(4)	V−N(4)	2.185(5)
V−N(2)	2.079(5)		
O(1)−V−N(4)	175.3(2)	V−N(2)−C(21)	130.5(4)
N(2)−V−N(3)	116.1(2)	O(1)*−V−O(1)	78.2(2)
O(1)*−V−N(2)	125.0(2)	V−O(1)−V*	101.8(2)
O(1)*−V−N(3)	118.3(2)		

During attempts to recrystallize **1** from toluene at room temperature, bright green crystals formed over a period of 2 weeks. The relatively insoluble product (**2**) is also paramagnetic, but its ^{19}F NMR spectrum in THF reveals that it is no longer C_3 symmetric; two types of C_6F_5 groups are observed in a 2:1 ratio, characteristic of a molecule with a mirror plane. The IR spectrum revealed absorptions at 3683 and 3453 cm^{-1} consistent with N−H vibrations. An X-ray study (Figure 2, Table 2) revealed that **2** is a V(IV) species containing a V_2O_2 core with one of the (protonated) arms of the $[N_3N_F]^{3-}$ ligand not coordinated. We speculate that **1** was oxidized to **2** by traces of water, as shown schematically in eq 2, even though the sample was kept in a drybox. However, the possible involvement of traces of oxygen cannot be excluded at this stage. We did not deliberately add known amounts of water or oxygen to **1**. Each vanadium in **2** has approximately a trigonal bipyramidal coordination geometry in which the two amido nitrogen atoms (N(2) and N(3)) and one oxygen (O(1)*) make up the trigonal plane; all $V{-}N_{eq}$ and $V{-}O_{eq}$ distances are in the range 1.91−1.95 Å. The other oxygen (O(1)) and the amine donor (N(4)) occupy apical coordination positions and have $V{-}N_{ax}$ and $V{-}O_{ax}$ distances that are approximately 0.1 Å longer than the $V{-}N_{eq}$ and $V{-}O_{eq}$ distances. The vanadium−vanadium distance (3.100 Å), V−O−V angle (101.8(2)°), O−V−O angle (78.2(2)°), and paramagnetic nature of **2** suggest that there is little interaction between the metals. No intermolecular hydrogen bonding was found. Compound **2** is similar to the recently published structure of $\{V(O)[N(SiMe_3)_2]_2\}_2$ in which the arrangement about each V is pseudotetrahedral.[22] In $\{V(O)[N(SiMe_3)_2]_2\}_2$, the V_2O_2 core is symmetric with $V\cdots V$ = 2.612(2) Å and V−O = 1.802(4) Å. The shorter bond lengths are to be expected in $\{V(O)[N(SiMe_3)_2]_2\}_2$ as a consequence of four-coordination about V versus five-coordination about V in **2**. Other examples of crystallographically characterized complexes that contain V_2O_2 cores are known,[23−25] but apparently $\{V(O)[N(SiMe_3)_2]_2\}_2$ is the only other divanadium(IV) species.

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In a typical divanadium(V) species the V_2O_2 core is even less symmetric than found in the divanadium(IV) species, although the V−O−V and O−V−O angles are similar to what is found in the divanadium(IV) species. In $\{VO_2F(bipy)\}_2$, for example,[23] the V−O distances are 1.691 and 2.361 Å and the V−O−V and O−V−O angles are 101.6 and 78.4°.

The "arm-off" feature of this molecule is what was found also in five-coordinate $[(C_6F_5NCH_2CH_2)_2N(CH_2CH_2NHC_6F_5)]Re(O)Cl$,[4] although the details could not be elucidated by X-ray crystallography as a consequence of a ligand disorder problem. Triamido ligands are prone to protonolysis, and the monoprotonated form found in **2** and $[(C_6F_5NCH_2CH_2)_2N(CH_2CH_2NHC_6F_5)]Re(O)Cl$ is the first stage of a process that ultimately would lead to the triamidoamine ligand being removed completely from the metal.

It is clear from this study and earlier study[7] that trigonal monopyramidal complexes of V(III) that contain triamidoamine ligands, at least the two that have been investigated so far, do not bind even traditionally strong π acceptors such as CO readily, let alone dinitrogen. It is also curious that no trigonal monopyramidal complex of a second- or third-row metal (e.g., Ta, Mo, W, or Re) has yet been isolated.[1] It is hoped that further studies of triamidoamine complexes of the heavier, earlier metals, especially Mo, will provide some answers as to why this is the case. We suspect that such species can attain the low-spin configuration, either prior to or during binding of a ligand in the apical position, and therefore are much more reactive.

Experimental Section

General experimental procedures and methods were analogous to those described elsewhere.[11]

$[N_3N_F]V$ (1). $[N_3N_F]VCl$ (0.62 mmol, 0.45 g) was added to a suspension of sodium amalgam (20 mg of Na in 3 g of Hg) in 15 mL of toluene at room temperature. The reaction mixture was stirred for 15 h and filtered through a pad of Celite. The solvents were removed in vacuo, and the resulting dark green solid was washed with pentane and dried in vacuo: yield 340 mg (80%); ^{19}F NMR (C_6D_6) δ −145 ppm (br s, 6), −179 ppm (br s, 3); no resonances were observed in ^1H NMR spectra; $\mu = 3.7$ at 22 °C (Evans method). Anal. Calcd for $C_{24}H_{12}F_{15}N_4V$: C, 41.64; H, 1.75; N, 8.09. Found: C, 41.37; H, 1.70; N, 8.21.

$[\{(C_6F_5NHCH_2CH_2)N(CH_2CH_2NC_6F_5)_2\}VO]_2$ (2). $[N_3N_F]V$ (0.110 g) was dissolved in minimum toluene (∼5 mL), and the solution was allowed to stand at room temperature in a closed vial in a nitrogen-filled drybox for ∼2 weeks. Bright green crystals of **2** (72 mg) were collected: yield 50%; ^{19}F NMR (C_6D_6) δ −150.1 (br s, 4), −158.9 (br s, 2), −165.9 (sharp, 2), −174.6 (sharp, 1), −175.2 ppm (sharp, 2); IR (Nujol, cm^{-1}) 3683, 3453.

Reaction of $[N_3N_F]V$ with Propylene Oxide. Propylene oxide (12 mg, 0.21 mmol) was added to a solution of $[N_3N_F]V$ (0.1 g, 0.14 mmol) in 15 mL of toluene. After 15 min the solvent was evaporated in vacuo, and the known vanadium(V) oxo complex,[11] $[N_3N_F]V{=}O$ (90 mg, 91%), was recovered and identified by NMR.

Description of the X-ray Study of $[(C_6F_5NCH_2CH_2)_3N]V$. The crystal was mounted under Paratone N and transferred to a Siemens Smart/CCD, three-circle (χ fixed at 54.78°) diffractometer equipped with a cold stream of N_2 gas. An initial unit cell was determined by harvesting reflections $I > 20\sigma I$ from 45 frames of 0.30 ω scan data with monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Crystal quality was checked by computing 3.0° rocking curves from which the ω width at half-height was found to be 0.23°. The data were collected using 0.30 ω scans. The data that were collected (5413 total reflections, 1261 unique, $R_{int} = 0.0611$) were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved (SHELXTL 5.0) by direct methods and standard difference Fourier techniques. Crystallographic data: formula, $C_{24}H_{12}F_{15}N_4V$; fw, 692.32; space group, $R\bar{3}$; $a = 14.40(2)$ Å, $b = 14.40(2)$ Å, $c = 21.84(4)$ Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$; $V = 3923(9)$ Å^3; $Z = 6$; $\rho_{Calcd} = 1.758$ g cm^{-3}; R_1 (all data) = 0.0697.

Description of the X-ray Study of $\{[(C_6F_5NHCH_2CH_2)(C_6F_5NCH_2CH_2)_2N]VO\}_2$. The crystal was mounted under Paratone N and transferred to a Siemens Smart/CCD, three-circle (χ fixed at 54.78°) diffractometer equipped with a cold stream of N_2 gas. An initial unit cell was determined by harvesting reflections $I > 20\sigma I$ from 45 frames of 0.30 ω scan data with monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Crystal quality was checked by computing 3.0° rocking curves from which the ω width at half-height was found to be 0.23°. The data were collected using 0.30 ω scans. The data that were collected (8293 total reflections, 3330 unique, $R_{int} = 0.0942$) were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved (SHELXTL 5.0) by direct methods and standard difference Fourier techniques. Crystallographic data: formula, $C_{24}H_{13}F_{15}N_4VO$; fw, 709.31, space group, $C2/c$, $a = 24.4401(4)$ Å, $b = 19.2403(4)$ Å, $c = 17.0602(2)$ Å; $\alpha = 90°$, $\beta = 116.3690(10)°$, $\gamma = 120°$; $V = 7187.6(2)$ Å^3; $Z = 8$; $\rho_{Calcd} = 1.309$ g cm^{-3}; R_1 (all data) = 0.0801.

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Supporting Information Available: An ORTEP drawing, crystal data and structural refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for both $[(C_6F_5NCH_2CH_2)_3N]V$ and $\{[(C_6F_5NHCH_2CH_2)(C_6F_5NCH_2CH_2)_2N]VO\}_2$ (11 pages). Ordering information is given on any current masthead page.

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