Formation of Bridging Nitride versus Terminal Oxovanadium Promoted by a Vanadium(II) Macrocyclic Complex

Jayne Jubb, Ludmila Scoles, Hilary Jenkins, and Sandro Gambarotta*

Abstract: The reaction of $[VCl_2(tmeda)_2]$ with the tetralithium salt of octaethylporphyrinogen $(oepg)[Li(thf)]_4$ initially yielded a monomeric V^{II} complex $[(oepg)VLi_4Cl_2(thf)_4]$ (**1**). Treatment of this species with tetramethylethylenediamine afforded a mixture from which $[(oepg)V(thf)_2][Li(tmeda)_2]\cdot 0.5$toluene (**2a**) (or **2b** when ethyl is replaced by *n*Pr) and the unprecedented nitrido-bridged dimeric species $[\{(oepg)V\}_2(\mu\text{-}N)(\mu\text{-}Li)_4][Li(tmeda)_2]$ (**3**) were isolated and characterized. The bridging nitrogen atom probably originated from the cleavage of dinitrogen, since the same reaction carried out under exclusion of N_2 gave $[(oepg)VO][Li(tmeda)]_2$ (**4**), where the oxo atom probably originated from deoxygenation of THF. The connectivity of **1**, **2b**, **3**, and **4** was demonstrated by X-ray analysis.

Keywords
bridging ligands · dinitrogen reduction · nitrides · vanadium complexes

Introduction

Ever since the discovery 30 years ago that the exceedingly inert dinitrogen molecule could form transition-metal complexes, research efforts have been centered on elucidating the factors affecting its coordination and activation.[1]

In this paper we describe the formation of a nitrido-bridged vanadium dimer probably obtained by dinitrogen cleavage performed by a low-valent oepg–vanadium complex (oepg = octaethylporphyrinogen). The decision to choose low-valent vanadium and a macrocyclic ligand to study dinitrogen activation was twofold. Firstly, low-valent vanadium in three different oxidation states has proven able to perform both fixation[2] and activation[3] of dinitrogen. In addition, vanadium is an important component of the vanadium nitrogenase cofactor,[4, 5] although the role of vanadium in this metalloenzyme is yet to be elucidated. Furthermore, a recent report has shown that the d^3 electronic configuration of a Mo^{III} species is sufficiently reactive to cleave the N–N triple bond and to generate the corresponding terminal and bridging nitride species.[6] The importance of these findings resides in the fact that nitrides are expected to be rather reactive functions and therefore are commonly regarded as promising intermediates for further functionalization and incorporation into organic substrates. Secondly, porphyrinogen ligands are able to enhance significantly the reactivity of low-valent transition metals and lanthanides towards a number of transformations[7] including dinitrogen reduction.[8] This implies that a V^{II} porphyrinogen complex could well be the type of system to interact with inert molecules such as dinitrogen and, given the electron-rich configuration, be the ideal substrate for reducing dinitrogen even further.

Experimental Section

All operations were performed under an inert atmosphere by means of standard Schlenk techniques. $[VCl_3(thf)_3]$ [9], [*trans*-$(tmeda)_2VCl_2$] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) [10], $OEPGH_4$ [11], and $(oepg)[Li(thf)]_4$ [12] were prepared according to published procedures. Li_3N (Aldrich) was used as received. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods [13], and corrections for underlying diamagnetism were applied to data [14]. Elemental analyses were carried out with a Perkin Elmer PE 2400 CHN analyzer. Ratios between heavy atoms were determined by X-ray fluorescence with a Philips 2400 instrument.

Preparation of $OPPGH_4$: A solution of pyrrole (15 mL, 0.21 mol) and 4-heptanone (30 mL, 0.21 mol) in absolute ethanol was refluxed for 2 h in the presence of a few drops of methanesulfonic acid, during which time a white microcrystalline solid separated. The dark mixture was cooled in an ice bath; the solid was collected by filtration and washed with absolute EtOH. The resulting solid was dried in vacuo for several hours (25 g, 0.038 mol, 73%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.10$ (brs, 1H; NH), 5.89–5.87 (pseudo-t, 2H; CH pyrrole), 1.67–1.57 (vbr, 4H; *n*Pr), 0.95 (vbr, 4H, *n*Pr), 0.80–0.77 (pseudo-d, 6H; *n*Pr); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 136.28$ (quaternary C), 104.53 (quaternary C), 42.65 (pyrrole ring), 40.12, 17.24, 14.50 (*n*Pr); Anal. calcd. (found) for $C_{44}H_{68}N_4$: C 80.92 (80.10), H 10.50 (10.41), N 8.58 (8.49).

Preparation of $(oppg)[Li(thf)]_4$: A solution of $OPPGH_4$ (8.5 g, 13 mmol) in THF (150 mL) was cooled to 0 °C. A solution of *n*BuLi in hexane (21 mL, 2.5 M, 0.052 mol) was added dropwise by syringe. A white solid started to separate and stirring was continued for two more hours at room temperature. The solvent was removed in vacuo and the white residue resuspended in hexane (100 mL). After stirring for 30 min the highly air-sensitive white microcrystalline material was collected by filtration and stored in a sealed ampoule under nitrogen (7 g, 7.2 mmol, 56%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 6.30$ (s, 2H; pyrrole), 3.3 (m, 4H; THF), 2.2 (brm, 4H; *n*Pr), 1.65 (brm, 4H; *n*Pr), 1.27 (m, 4H; THF), 1.01 (pseudo-t, 6H; *n*Pr).

Preparation of $[(oepg)VLi_4Cl_2(thf)_4]$ (1): The addition of $[VCl_2(tmeda)_2]$ (1 g, 2.8 mmol) to a solution of $(oepg)[Li(thf)]_4$ (2.7 g, 3.1 mmol) in toluene (100 mL) yielded a greenish-brown suspension with a rather large amount of very air-sensitive yellow microcrystalline solid. The solid was transferred to a continuous extraction apparatus and extracted with boiling THF to eliminate LiCl. The THF solution was allowed to stand overnight at −30 °C, upon which yellow prisms of **1** separated

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(1.75 g, 1.8 mmol, 64%). IR (Nujol): $\tilde{\nu}$ = 3085 (w), 1333 (s), 1060 (s), 1046 (vs), 900 (m), 882 (s), 855 (m), 850 (m), 769 (s), 745 (m), 700 (w), 699 (w) cm^{-1}; Anal. calcd. (found) for $C_{52}H_{80}N_4VO_4Li_4Cl_2$: C 64.07 (64.00), H 8.27 (8.11), N 5.75 (5.69); experimental V:Cl ratio 1:1.97; μ_{eff} = 3.79 μ_B.

Preparation of [(oepg)V(thf)$_2$][Li(tmeda)$_2$]·0.5 toluene (2a): The greenish-brown slurry obtained by reaction of [VCl$_2$(tmeda)$_2$] (1.53 g, 4.3 mmol) with (oepg)[Li(thf)]$_4$ (3.82 g, 4.4 mmol) in THF (100 mL) was stirred for two days at room temperature. The addition of TMEDA (3 mL) to the suspension darkened the color and partially dissolved the yellow microcrystalline solid. After removal of the insoluble material by filtration, the red-brown solution was evaporated to dryness and the residual solid redissolved in toluene. After further filtration, the solution was concentrated. Upon allowing the resulting solution to stand for two days at room temperature red crystals of **2a** separated (1.8 g, 0.9 mmol, 20%). IR (Nujol): $\tilde{\nu}$ = 3085 (w), 1575 (vb), 1305 (w), 1291 (m), 1255 (w), 1243 (w), 1158 (w), 1125 (w), 1120 (w), 1059 (s), 1038 (s), 1025 (s), 1012 (s), 947 (w), 925 (w), 900 (w), 851 (m), 793 (m), 735 (s), 700 (w) cm^{-1}; Anal. calcd. (found) for $C_{119}H_{200}N_{16}V_2O_4Li_2$: C 70.24 (69.99), H 9.91 (9.89), N 11.01 (10.91); experimental V:Cl ratio 1:0.07; μ_{eff} = 2.77 μ_B.

Preparation of [(oppg)V(thf)$_2$][Li(tmeda)$_2$]·0.5 toluene (2b):

Method A: The addition of [VCl$_2$(tmeda)] (0.7 g, 4.59 mmol) to a suspension of (oppg)[Li(thf)]$_4$ (4.43 g, 4.59 mmol) in toluene (100 mL) yielded a forest-green mixture. The reaction mixture was stirred under nitrogen for 2 h and stirring was continued overnight. Treatment of the resultant green-yellow slurry with excess TMEDA (4 mL) darkened the color. The mixture was stirred for an additional 2 h, then boiled and filtered while hot. The solution was concentrated in vacuo and allowed to stand at room temperature for 2 d, yielding well-formed red crystals of **2b** (0.9 g, 0.4 mmol, 9%) IR (Nujol): $\tilde{\nu}$ = 3102 (m), 1584 (br,w), 1285 (s), 1242 (w), 1200 (w), 1170 (w), 1147 (w), 1125 (m), 1060 (s), 1023 (s), 937(m), 879 (m), 786 (m), 732 (vs), 618 (m), 570 (w) cm^{-1}. Anal. calcd. (found) for $C_{135}H_{232}N_{16}V_2O_4Li_2$: C 71.77 (71.69), H 10.35 (9.99), N 9.92 (9.78); experimental V:Cl ratio 1:0.00; μ_{eff} = 2.81 μ_B.

Method B: *n*BuLi (11.8 mL, 2.5 M, 29.4 mmol) was added dropwise to a suspension of OPPG (4.80 g, 7.35 mmol) in hexane (150 mL) at 0 °C. The mixture was warmed to room temperature, stirred overnight, then refluxed for 30 min to yield a pale yellow suspension. The solvent was removed in vacuo to leave a pale yellow solid, which was redissolved in toluene (150 mL) followed by the addition of TMEDA (2.2 mL, 14.7 mmol) and [VCl$_3$(thf)$_3$] (2.75 g, 7.35 mmol). The resultant dark red-brown solution was stirred overnight and filtered, and the volume reduced to ca. 50 mL. After standing for 3 d at room temperature, large red crystals of **2b** separated (4.0 g, 3.2 mmol, 44%).

Preparation of [{(oepg)VLi$_2$}$_2$(μ-N)][Li(tmeda)$_2$] (3):

Method A: [VCl$_2$(tmeda)$_2$] (1.0 g, 2.8 mmol) was added to freshly distilled anhydrous toluene (150 mL) containing the porphyrinogen tetralithium salt [Li$_4$(oepg)(thf)$_4$] (2.7 g, 3.1 mmol) and a slight excess of TMEDA (1 mL). After stirring overnight at room temperature, the solution was filtered and the red-brown filtrate allowed to stand at room temperature. After 2 weeks, very air-sensitive blue needles of **3** (0.3 g, 0.22 mmol, 16%) were isolated by filtration. The mother liquor was evaporated to dryness and the residual solid extracted with boiling hexane, yielding an additional crop of crystals (total yield 25%). IR (Nujol): $\tilde{\nu}$ = 1321 (m), 1288 (m), 1261 (m), 1245 (m), 1205 (w), 1172 (w), 1159 (w), 1128 (w), 1097 (w), 1068 (m), 1051 (s), 1030 (s), 972 (m), 946 (m), 925 (m), 887 (m), 848 (m), 789 (m), 761 (s), 744 (s), 590 (w), 567 (w), 492 (m), 438 (m) cm^{-1}; μ_{eff} = 2.85 μ_B (per dimer); Anal. calcd. (found) for $C_{84}H_{128}V_2N_{13}Li_5$: C 69.26 (69.11), H 8.86 (8.78), N 12.50 (12.46).

Method B: A bright red solution of **2a** (0.7 g, 0.7 mmol) in THF (50 mL) was boiled and stirred with an excess of Li$_3$N for 4 d. The color of the solution slowly turned brownish, and blue microcrystalline **3** started to separate. The crude solid was purified by continuous extraction in hexane, yielding blue microcrystals of analytically pure **3** (0.23 g, 0.16 mmol, 45%).

Preparation of [(oepg)V(O)Li$_2$] (4): [VCl$_2$(tmeda)$_2$] (2.57 g, 7.25 mmol) and the tetralithium salt [Li$_4$(oepg)(thf)$_4$] (6.24 g, 7.31 mmmol) were stirred at room temperature overnight in anhydrous THF (250 mL) and under argon atmosphere. After being boiled overnight, the red-brown reaction mixture was evaporated to dryness and the residue extracted overnight with boiling hexane (300 mL). The blue microcrystalline solid formed was filtered off and the maroon filtrate left to stand at −30 °C overnight, affording green moderately air-stable cubic crystals of **4** (1.01 g, 1.2 mmol, 16%). IR (Nujol): $\tilde{\nu}$ = 3085 (w), 1615 (vb,w), 1314 (s), 1301 (w), 1281 (s), 1225 (m), 1159 (w), 1147 (m), 1126 (w), 1070 (s), 1032 (m), 1012 (m), 982 (s), 949 (m), 925 (w), 885 (w), 859 (m), 794 (m), 759 (m), 740 (m), 678 (w), 584 (m) cm^{-1}; μ_{eff} = 1.77 μ_B; Anal. calcd. (found) for $C_{48}H_{80}VOLi_2N_8$: C 67.82 (67.77), H 9.49 (9.41), N 13.18 (13.14).

X-ray crystallography [15]: Data were collected at temperatures in the range −157 – −160 °C by means of the ω-2θ scan technique in the range $3.5 < 2\theta < 50.0°$, for suitable air-sensitive crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects but no absorption corrections were necessary. The structures were solved by either Patterson or direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined with one common thermal parameter. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with [I > 2.5σ(I)]. Neutral atomic scattering factors were taken from Cromer and Waber [16]. Anomalous dispersion effects were included in F_{calcd}. All calculations were performed with the TEXSAN package on a Digital VAX station. Details of data collection and structure refinement are reported in Table 1. Selected bond lengths and angles are given in Table 2.

Table 1. Crystal data and structural analysis results.

	1	**3**	**4**
formula	$C_{52}H_{80}N_4Li_4VCl_2O_4$	$C_{84}H_{128}V_2N_{13}Li_5$	$C_{48}H_{80}VOLi_2N_8$
M_r	974.84	1456.61	850.04
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/c$
a (Å)	11.608(1)	25.797(1)	12.9825(9)
b (Å)	12.163(1)	13.548(2)	18.7729(6)
c (Å)	11.405(1)	24.217(1)	19.982(1)
α (°)	108.98(1)		
β (°)	96.78(1)	109.338(9)	95.293(7)
γ (°)	115.86(2)		
V (Å^3)	1304.7(8)	7986(2)	4849.4(8)
Z	1	4	4
radiation (Mo$_{K\alpha}$, Å)	0.71069	0.71069	0.71069
T (°C)	−144	−155	−155
d_{calcd} (g cm^{-3})	1.241	1.211	1.164
μ_{calcd} (cm^{-1})	3.31	2.75	2.37
no. obs.	3025	5028	4005
no. parameters	303	464	541
R, R_w [a]	0.048, 0.066	0.044, 0.054	0.051, 0.064

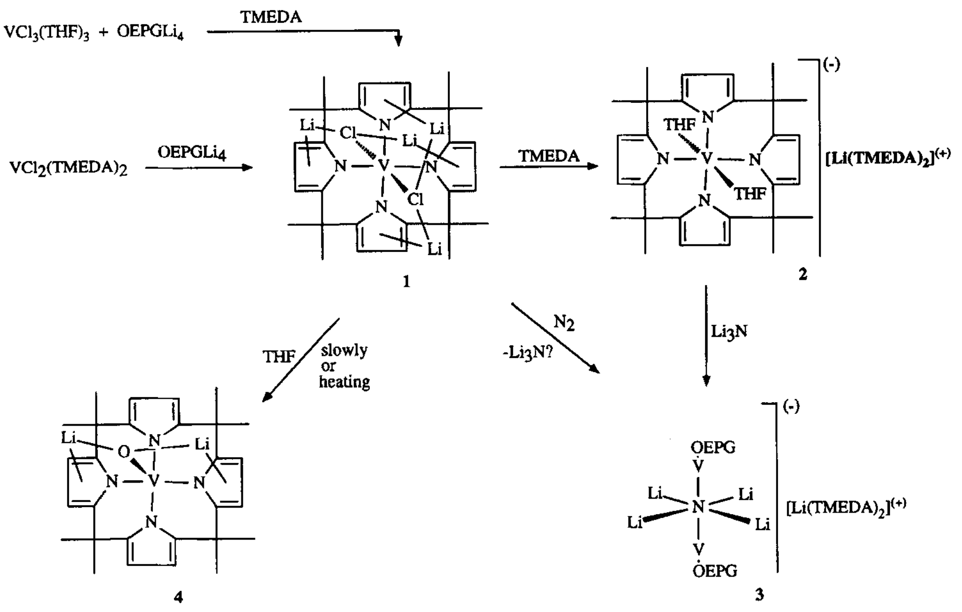
[a] $R = \sum||F_0| - |F_c||/\sum|F_0|$; $R_w = [(\sum w(|F_0| - |F_c|)^2/\sum wF_0^2)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°).

1		**3**		**4**	
V1–Cl1	2.6510(9)	V1–N1	2.150(2)	V1–O1	1.597(3)
V1–N1	2.133(3)	V1–N2	2.146(2)	V1–N1	2.049(4)
V1–N2	2.135(3)	V1–N5	2.150(2)	V1–N2	2.078(4)
Li1–Cl1	2.350(6)	V1–N4	2.150(2)	V1–N3	2.052(4)
Li2–Cl1	2.327(6)	V1–N7	1.8499(5)	V1–N3	2.052(4)
Li1–N1	2.259(6)	Li2–N5	2.168(5)	V1–N4	2.076(4)
Li1–C1	2.291(7)	Li2–N7	2.217(5)	N1-V1-N2	85.1(1)
Li1–C2	2.350(7)	Li3–N2	2.318(6)	N2-V1-N3	88.4(1)
Li1–C3	2.346(7)	Li3–N7	2.599(5)	N1-V1-N3	149.5(1)
Li1–C4	2.281(7)	Li3–C6	2.366(6)	N1-V1-O1	105.7(2)
Li1–O1	1.938(6)	Li3–C7	2.370(6)	N2-V1-O1	102.0(2)
N1-V1-N2	91.2(1)	Li3–C19	2.363(6)		
Cl1-V1-N1	95.46(7)	N1-V1-N2	156.01(8)		
Cl1-V1-N2	84.95(7)	N1-V1-N5	88.29(8)		
Li1-Cl1-Li2	98.1(2)	N1-V1-N4	86.73(8)		
		N1-V1-N7	102.35(6)		
		N2-V1-N7	101.57(6)		
		V1-N7-Li2	86.8(1)		
		V1-N7-Li3	89.6(1)		
		Li2-N7-Li3	90.2(1)		

Results and Discussion

The reaction in toluene of the tetralithium salt of octaethylporphyrinogen [(oepg)Li$_4$(thf)$_4$] with [VCl$_2$(tmeda)$_2$] resulted in the formation of a very air-sensitive yellow microcrystalline solid in good yield (Scheme 1). Continuous extraction in THF yielded well-formed yellow crystals of [(oepg)VLi$_4$Cl$_2$(thf)$_4$] (**1**), the formulation of which was indicated by combustion analysis, atomic absorption, and X-ray fluorescence data. The magnetic



Scheme 1.

moment [$\mu_{\text{eff}} = 3.79\mu_B$] was also consistent with the expected d^3 electronic configuration of V$^{\text{II}}$ based on the proposed formulation.

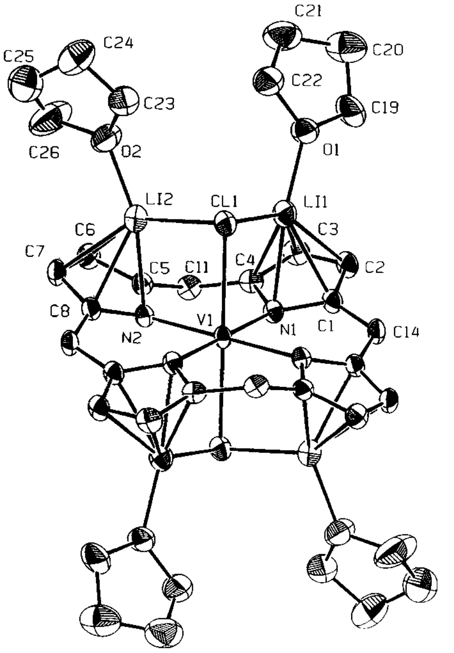


Fig. 1. ORTEP plot of **1**. Thermal ellipsoids are drawn at the 50% probability level. Alkyl groups have been removed for clarity.

The molecular connectivity of **1** was elucidated by an X-ray crystal structure (Fig. 1). The complex is monomeric and consists of a vanadium atom that lies on a center of symmetry and is surrounded by four nearly coplanar nitrogen atoms of the macrocycle [V1–N1 = 2.133(3) Å, V1–N2 = 2.135(3) Å, N1-V1-N2 = 91.2(1)°, N1-V1-N2a = 88.8(1)°]. The octahedral coordination geometry of the vanadium atom is completed by two chlorine atoms [V1–Cl1 = 2.6510(9) Å] in *trans* positions with respect to vanadium and located on the axis perpendicular to the plane of the macrocycle [Cl1-V1-N1 = 95.46(7)°, Cl1-V1-N2 = 95.46(7)°]. Four lithium atoms are bonded to the four pyrrole rings in an η^5-bonding fashion [Li1–N1 = 2.259(6) Å, Li1–C1 = 2.291(7) Å, Li1–C2 = 2.350(7) Å]. The lithium cations are placed two by two on the two sides of the macrocyclic plane and are also connected to the two chlorine atoms [Li1–Cl1 = 2.350(6) Å, Li2–Cl1 = 2.327(6) Å] forming bent Li-Cl-Li arrays [Li1-Cl1-Li2 = 98.1(2)°]. One molecule of THF completes the coordination sphere of each lithium atom.

Attempts to remove the two LiCl units from complex **1** by reaction with TMEDA (usually a powerful scavenger for lithium cations) resulted in a complicated reaction. After addition of excess TMEDA to a suspension of **1**, the color darkened and the yellow complex **1** dissolved. The resulting red solution yielded shiny red crystals of a new complex formulated as [(oepg)V(thf)$_2$][Li(tmeda)$_2$]·0.5(toluene) (**2a**) on the basis of combustion analysis data. Magnetic measurements were also consistent with a d^2 electronic configuration of a V$^{\text{III}}$ metal center. Although crystals suitable for X-ray analysis could not be grown for this species, the OPPG derivative **2b** (OPPG = octapropylporphyrinogen) yielded sufficiently large crystals of a compound of the same color and with analytical data which indicated the same formulation. Complex **2b** was also conveniently synthesized to a large scale and in moderate yield by direct reaction of [VCl$_3$(thf)$_3$] with [(oppg)Li$_4$] in the presence of TMEDA. Complexes **2** are thermally robust and can be refluxed for two weeks in THF without decomposition or reaction.

The X-ray crystal structure determination of **2b** was unfortunately hampered by difficulties such as poor scattering which, in addition to the unusually large cell dimensions, required processing of a very large number of reflections and resulted in a rather high value of the agreement factors.[17] Nevertheless, the structure was of sufficient quality to demonstrate the formula and to elucidate the chemical connectivity.

The formation of the trivalent **2** from the divalent yellow **1** involves a redox reaction. The fact that this species is formed in a rather low yield indicates that another compound might be formed during the reaction triggered by TMEDA. In fact, an intensely blue, insoluble, paramagnetic and extremely air-sensitive complex **3** was obtained after isolating complex **2b** and allowing the mother liquor to stand at room temperature for a few days. Combustion analysis data suggested the formulation [{(oepg)VLi$_2$}$_2$(μ-N)][Li(tmeda)$_2$] (**3**). Even though it was obtained in very low yield, the formation of **3** is a completely reproducible process. The yield of **3** was increased up to 25% by evaporating the toluene reaction mixture to dryness, and extracting the resulting residue overnight with boiling hexane.

The X-ray crystal structure of **3** revealed a dimeric anionic complex and a [Li(tmeda)$_2$] countercation (Fig. 2). The anionic unit is composed of two identical and parallel (oepg)V moieties with the two vanadium atoms connected by a bridging nitride. The V–N distance [V1–N7 = 1.8499(5) Å] is rather long but still in the range of distances displayed by other vanadium or

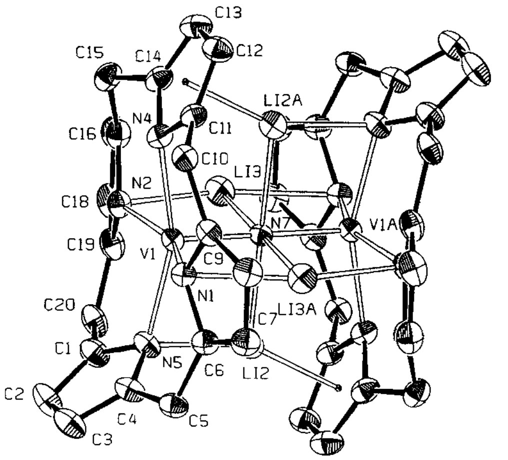


Fig. 2. ORTEP plot of the anionic moiety of **3**. Thermal ellipsoids are drawn at the 50% probability level. Alkyl groups have been removed for clarity.

first-row transition metal nitride species (typical V–N distance range 1.55–1.96 Å).[18] The four lithium atoms and the two vanadium atoms form an octahedron centered on the nitride, which is placed between the two porphyrinogen rings [Li2–N7 = 2.217(5) Å, Li3–N7 = 2.599(5) Å, Li2-N7-Li3 = 90.2(1)°, V1-N7-Li2 = 86.8(1)°, V1-N7-Li2a = 93.2(1)°].

The magnetic moment of **3** [$\mu_{\text{eff}} = 2.85\ \mu_B$ per dimer] was significantly lower than expected for the d^2 electronic configuration of a V^{III} center. However, the rather close proximity of the two metal centers, in addition to the presence of a bridging nitride, may possibly account for the existence of significant magnetic coupling between the two vanadium centers. In spite of being paramagnetic, the complex was EPR-silent in both solid state (powder and single crystal) and solution.

The refinement of the structure of **3** unambiguously identified the bridging central atom as a nitride. Protonolysis of **3** with 11 equivalents of gaseous HCl and subsequent attempts to identify ammonia were unsuccessful due to the presence of TMEDA, which interfered with the Nessler reagent tests and hampered its determination by UV[19] and other microanalytical tests.[20] However, the existence of a nitride was conclusively proved by the successful direct synthesis of complex **3** by reaction of **2** with Li_3N through a clean, albeit very slow, reaction (4 d in refluxing THF) (Scheme 1). It should be remembered that complexes **2** are thermally stable and did not undergo any reaction or decomposition in the absence of Li_3N even after refluxing for two weeks in THF.

Even if dinitrogen appears to be the most obvious source of the nitride, this could not be proved by NMR, IR, or MS since spectra were largely uninformative because of the paramagnetism and the presence of considerably complicated spectroscopic patterns, which rendered the results of labeling isotope experiments with $^{15}N_2$ inconclusive. Nevertheless, the fact that reactions carried out under argon gave only the red compound **2** together with a variable amount of a new green vanadyl compound **4** (vide infra) and no trace of complex **3** strongly indicates that dinitrogen is indeed the source of the bridging nitride atom. However, at this stage we cannot conclusively exclude the possibility that the oepg ligand might also be the source of the bridging nitride.

The fact that complex **3** can be conveniently prepared by means of the direct reaction of **2** with Li_3N suggests a reason for the concomitant formation of trivalent **2** and **3** upon treatment of divalent **1** with TMEDA. The complete reduction of one molecule of N_2 to two N^{3-} requires that a total of six electrons be transferred to N_2. Since the reaction is initiated by the treatment of complex **1** with TMEDA, the first step of the process may be regarded as the formal abstraction of LiCl and consequent formation of a highly reactive and coordinatively unsaturated V^{II} "[(oepg)VLi$_2$]" intermediate. Not surprisingly, the divalent vanadium metal center possesses sufficient reactivity to interact with N_2.[2] Formally, the reduction of N_2 by 6 molecules of **1** produces two nitrides. Six alkali cations together with 6 molecules of **2** are also formed by the reaction. Formally, addition of two molecules of Li_3N to four of the six molecules of **2** produces 2 equivalents of complex **3**, leaving behind two unreacted molecules of **2** (Chart 1).

As mentioned above, complex **1** is stable in the solid state while stored under nitrogen or argon. Nevertheless, it slowly decomposes in THF, where it produces the paramagnetic [(oepg)V(O)Li$_2$] (**4**), which can be separated as a green crystalline solid. Reactions of **1** with TMEDA carried out under more drastic conditions (continuous extraction of the reaction residue with hexane) and in the absence of dinitrogen in the reaction medium, also gave, in addition to the usual complex **2**, the new bright green species **4**. The IR spectrum of **4** showed the characteristic resonance of the vanadyl group as a strong band at 982 cm^{-1}, the presence of which was confirmed crystallographically (vide infra). Complex **4** is paramagnetic and both solid-state Gouy and solution Evans method measurements of the magnetic susceptibility were in agreement with a d^1 electronic configuration of V^{IV} based on the formula provided by combustion analysis data. The X-ray fluorescence spectrum showed the presence of only traces of chlorine. The EPR spectrum in both solid state and solution showed the characteristic eight-line spectrum.

The X-ray structure of **4** comprised a porphyrinogen ligand in the usual saddle-shape conformation (Fig. 3), which surrounds a V=O [V1–O1 = 1.597(3) Å] moiety and confers a square pyramidal coordination geometry on the metal center [V1–N1 = 2.049(4) Å, V1–N2 = 2.078(4) Å, N1-V1-N2 = 85.1(1)°, N1-V1-N3 = 149.5(1)°, N1-V1-O1 = 105.7(2)°]. Two lithium cations were found to be coordinated to two of the four pyrrole rings in the usual η^5 fashion [Li1–N4 = 2.473(7) Å, Li1–C16 = 2.391(9) Å, Li1–C17 = 2.313(9) Å] and are positioned on the same side as the vanadyl oxygen atom, forming long bonding contacts with it [Li1···O1 = 3.557(8) Å, Li1-O1-Li2 = 176.9(2)°].

It seems plausible that the vanadyl group originates from the deoxygenation of THF by complex **1**, since complex **4** was not

$$\underset{\mathbf{1}}{6[(\text{oepg})\text{VLi}_2(\text{LiCl})_2]} \xrightarrow{-12\,\text{LiCl}} 6\text{``}[(\text{oepg})\text{VLi}_2]\text{''} \xrightarrow{\text{TMEDA}} \underset{\mathbf{2}}{6[(\text{oepg})\text{V(thf)}_2][\text{Li(tmeda)}_2]} + 6\,e^- + 6\,\text{Li}^+$$

$$\text{N}_2 + 6\,e^- \longrightarrow 2\,\text{N}^{3-}$$

$$6[(\text{oepg})\text{V(thf)}_2][\text{Li(tmeda)}_2] + 2\,\text{N}^{3-} + 6\,\text{Li}^+ \longrightarrow 2[(\text{oepg})\text{V(thf)}_2][\text{Li(tmeda)}_2] + 2[\{(\text{oepg})\text{V-N-V(oepg)}\}\text{Li}_4][\text{Li(tmeda)}_2]$$

$$\underset{\mathbf{1}}{6[(\text{oepg})\text{VLi}_2(\text{LiCl})_2]} + \text{N}_2 \longrightarrow \underset{\mathbf{2}}{2[(\text{oepg})\text{V(thf)}_2][\text{Li(tmeda)}_2]} + \underset{\mathbf{3}}{2[\{(\text{oepg})\text{V-N-V(oepg)}\}\text{Li}_4][\text{Li(tmeda)}_2]}$$

Scheme 2.

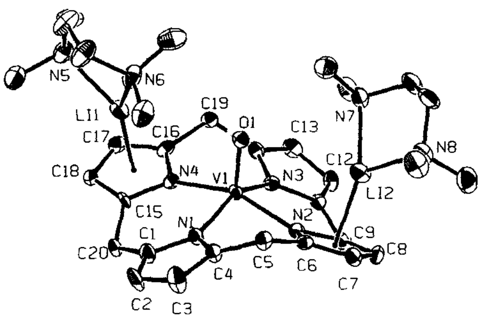


Fig. 3. ORTEP plot of **4**. Thermal ellipsoids are drawn at the 50% probability level. Alkyl groups have been removed for clarity.

formed when the reactions were carried out in hydrocarbon solvents or pyridine. This behavior is not particularly surprising given the fact that previous attempts to prepare V^{III} complexes of OEPG invariably led to different types of fragmentation of THF depending on the amount of THF available to the vanadium center.[7] In these reactions the fragmentation of THF is merely driven by the Lewis acidity of the system and does not involve a change of the formal oxidation state of the metal. Accordingly, reaction of $[VCl_3(thf)_3]$ with $[(oepg)Li_4]$ in toluene, but in the presence of TMEDA, gave **2** in acceptable yield with no indication that the other species arising from THF fragmentation were formed. In contrast, in the case of the divalent **1** the vanadium center might be able, while in combination with nitrogen-based donor ligands, to deoxygenate THF by a redox mechanism. In agreement with this hypothesis, ethylene, ethane, butane, and 1-butene were identified in the reaction mixture by GCMS.

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