

***trans*-[Na(thf)][V(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂]: Structural Characterization of a Dinitrogenvanadium Complex, a Functional Model for Vanadiumnitrogenase**

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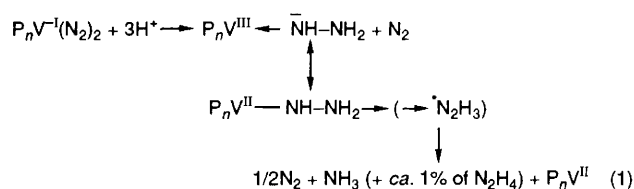
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Reduction of VCl₃(thf)₃ (thf = tetrahydrofuran) by Na in the presence of bis(phosphines) and N₂ yields the complexes *trans*-[V(N₂)₂L₂]⁻, which have been structurally characterized by X-ray crystallography for L = Ph₂PCH₂CH₂PPh₂, and in solution by ⁵¹V NMR spectroscopy for L = Me₂PCH₂CH₂PMe₂; 25% of the coordinated N₂ is reductively protonated to NH₃ and a small amount of N₂H₄ by HBr.

The discovery and first characterization of an alternative, *i.e.* vanadium-containing nitrogenase (V-nase) encoded along with the common molybdenum nitrogenase in nitrogen-fixing bacteria such as *Azotobacter*¹ and *Anabaena*² has prompted investigations into the chemistry, structure and function of vanadium complexes containing dinitrogen fragments either in the form of formally neutral N₂ or in reduced (and protonated) states. Examples are [V(CO)₅N₂]⁻,³ which is stable in solution and below 220 K only, and hydrazine complexes of the general formula η⁵-C₅H₅V(CO)₃ hydrazine.⁴ More recently, a dinuclear compound of composition [(py)VL₂]₂μ-N₂ [where L is *o*-(Me₂NCH₂)C₆H₄] has been structurally characterized by Gambarotta *et al.*⁵ The N-N bond length in this complex is 1.228(4) Å [d(NN) in free nitrogen: 1.098 Å]. The compound should hence be considered to be a diazene rather than a dinitrogen complex. It has been demonstrated by Leigh *et al.*⁶ that half of the N₂ can be converted into NH₃ on treatment with acids. Nevertheless, the compound is of restricted value as a model, since it is not likely, in the light of recent structural evidence for molybdenum nitrogenase,⁷ that the FeVa-cofactor in vanadium-nitrogenase contains two closely linked vanadium centres.

While dinitrogen complexes of molybdenum(0), stabilized by phosphines, and containing the N₂ ligand in the end-on coordination mode have been known⁸ and thoroughly investigated⁹ for more than two decades, only a singular account on the corresponding, valence-isoelectronic vanadium(-I) complexes, elucidating spectroscopic characteristics, has so far

appeared.¹⁰ We have now been able to grow crystals of one of the basic complexes, *viz.* [Na(thf)][V(N₂)₂(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂), [Na(thf)]-1,† and to determine the



† *Preparation of 1*: 370 mg of VCl₃(thf)₃ (1 mmol) and 800 mg of dppe (2 mmol) were dissolved in 20 ml of dry, oxygen-free thf, cooled to -78 °C and treated with 200 mg of freshly prepared and finely divided sodium sand and 20 mg of naphthalene. The Schlenk tube was connected to a N₂ source, and the suspension stirred for 1 day at -78 °C, and for an additional day at -40 °C. A dark, reddish-brown solution formed *via* a blue intermediate (a V^{II}-phosphine complex), which was passed through 1 cm of celite in the cold. Treatment with 50 ml of pre-cooled hexane led to a brown precipitate of [Na(thf)]-1. This was filtered off and dried by passing cold N₂ through the residue on the filter plate. Yield 750 mg (81%). IR (nujol mull): ν(NN) = 1790 cm⁻¹. ⁵¹V NMR (thf, 250 K, relative VOCl₃): δ = -746 (broad, unresolved signal). At room temp., solutions containing 1 decompose within a few days. Crystals of 1 (0.4 × 0.2 × 0.15 mm³) were obtained by allowing a saturated thf-hexane solution of 1 to stand at -78 °C for ca. 1 week.

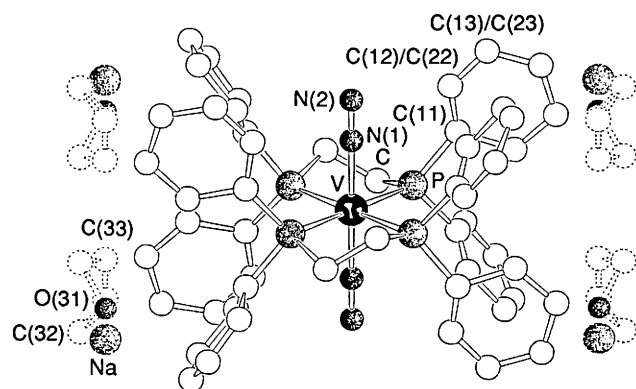


Fig. 1 SCHAKAL plot of $[\text{Na}(\text{thf})]\text{-1}$. The space group is $Immm$. Atoms defining the asymmetric unit are numbered. The octahedral $\text{V}(\text{N}_2)_2\text{P}_4$ core of the anion is emphasized by shaded calottes. The phenyl rings and the ethylene back-bone are disordered. The cation $[\text{Na}(\text{thf})]^+$ (thf is disordered) is statistically distributed between four equivalent site positions. There is a bonding interaction between Na^+ and $\text{N}(2)$ with formation of a $\text{V}-\text{N}\equiv\text{N}\cdots\text{Na}$ bridge. Selected distances (Å) and angles ($^\circ$): $\text{V}-\text{N}(1)$ 1.915(11), $\text{N}(1)-\text{N}(2)$ 1.130(16), $\text{V}-\text{P}$ 2.419(3), $\text{P}-\text{C}$ 1.829(12), $\text{P}-\text{C}(11)$ 1.816(8), $\text{Na}\cdots\text{N}2$ 2.445(11), $\text{Na}\cdots\text{O}31$ 2.349(12); $\text{N}(1)-\text{V}-\text{P}$ 90.0(0), $\text{V}-\text{N}(1)-\text{N}(2)$ 180.0(30), $\text{C}-\text{P}-\text{C}(11)$ 110.6(5), $\text{V}-\text{P}-\text{C}$ 108.2(4), $\text{V}-\text{P}-\text{C}(11)$ 122.7(3).

crystal and molecular structures by X-ray diffraction analysis. \ddagger

The structure of $[\text{Na}(\text{thf})]\text{-1}$ (Fig. 1) was solved and refined in the space group $Immm$. Regarding the anion **1**, the asymmetric unit is defined by the atoms V, N(1), N(2), C, P, C(11) and C(12) [C(22)] to C(16)[C(26)]. The overall structure and the bonding parameters of **1** (for a selection see legend to Fig. 1) are very much the same as for the neutral molybdenum complex $\text{trans}[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$.¹¹ The counter ion Na^+ has bonding contacts to the tetrahydrofuran oxygen [$d(\text{Na}-\text{O}) = 2.35$ Å]. There is also a non-negligible contact between sodium and the terminal nitrogen of **1** [$d(\text{Na}-\text{N}(2)) = 2.45$ Å], hence a contact-ion pair interaction through a $\text{V}-\text{N}\equiv\text{N}\cdots\text{Na}$ bridge.

This structure of the anion is also preserved in thf solution, as shown in Fig. 2, depicting the ^{51}V NMR spectrum of $\text{trans}[\text{V}(\text{N}_2)_2(\text{dmpe})_2]^-$, **2**, ($\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$). The spectrum shows a well-resolved quintet [$^1J(^{31}\text{P}-^{51}\text{V})$ coupling] of triplets [$^1J(^{15}\text{N}-^{51}\text{V})$ coupling].

As dry **Na-1** or **Na-2** is treated with an excess of HBr , one of the four nitrogens is converted into NH_4^+ . A small amount of hydrazine is also formed. No hydrogen, an important additional product in natural nitrogen fixation by V-nase, has been detected. Small but significant amounts of free N_2H_4 are also

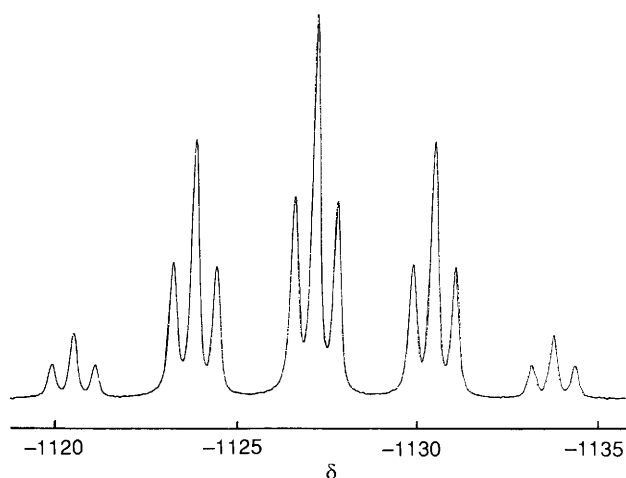


Fig. 2 93.7 MHz ^{51}V NMR spectrum of **2**. $\delta(^{51}\text{V}) = -1123$ (relative to VOCl_3), $J(^{51}\text{V}-^{31}\text{P}) = 314$, $J(^{51}\text{V}-^{15}\text{N}) = 57$ Hz

produced during N_2 reduction by V-nase.¹² The electrons in this reductive protonation are delivered by V^{-1} , which is converted to chlorophosphine vanadium complexes of, according to oxidimetric titration, V^{II} and small but varying amounts of V^{III} . Compounds **1** and **2** may hence be considered functional models of the nitrogenase activity of V-nase. The overall balance can be represented by eqn. (1).

Eqn. (1) incorporates some aspects of a tentative mechanism for NH_3 production, based on the assumption that a hydrazido(1-) and a hydrazinyl intermediate are formed, with concomitant disproportionation of the latter. Complexes containing the N_2H_3 (hydrazinyl) radical have recently been characterized.^{13,14} Investigations to further elucidate this mechanism are presently under way.

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\ddagger Crystal data: $\text{C}_{56}\text{H}_{56}\text{N}_4\text{NaOP}_4\text{V}$, $M = 998.92$ g mol $^{-1}$, orthorhombic, space group $Immm$, $a = 10.980(1)$, $b = 12.678(1)$, $c = 19.755(3)$ Å, $Z = 2$, $V = 2750.0(6)$ Å 3 , $D_c = 1.206$ g cm $^{-3}$, $F(000) = 1012$, $\mu(\text{Cu}-\text{K}\alpha_1) = 29$ cm $^{-1}$. Final $R = 0.095$ ($R_w = 0.094$) for 828 significant reflections with $F_o > 4\sigma(F_o)$, measured in the θ range 2.25–60.0 $^\circ$ at room temp. on a Enraf Nonius CAD4 diffractometer. Number of refined parameters = 165. Residual electron density: max. 0.66, min. -1.09 e Å $^{-3}$. The structure was solved and refined in the space group of highest symmetry ($Immm$) among those fitting the extinction conditions. The positions of V and P were obtained from a Patterson synthesis; the final difference Fourier gave the positions of the remaining non-hydrogen atoms. A model was developed, where the phenyl rings of the asymmetric unit exhibit a 1:1 disorder. The symmetry operations generated an additional disorder of the ethylene back-bone of dppe, the thf, and the site occupancies of the cation $\text{Na}(\text{thf})$. The hydrogen atoms were calculated into ideal positions and refined in the last cycle with isotropic temperature factors. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.