Hydrazine complexes of vanadium(II and III)

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Abstract

The reaction of $VCl_3(thf)_3$ (**1**) with *N,N*-dimethylhydrazine yields $VCl_3(thf)_2(H_2NNMe_2)$ (**2**) or, with excess hydrazine, $VCl_3(NH_2NMe_2)_2$ (**4**). In the presence of 1,2-bis(dimethylphosphino)ethane (dmpe), $VCl_3(dmpe)(NH_2NMe_2)\cdot 0.5thf$ (**7**) is obtained. As **1** is reacted with tris(3-dimethylphosphinopropyl)phosphine (tdmp) and lithium hydrazide, the V^{II} species $VCl_2(tdmp)(NH_2NMe_2)$ (**10**) and $VCl_2(tdmp)$ (**11**) are formed. While H_2NNMe_2 coordinates end-on via its NH_2 group in the case of **2, 7** and **10, 4** probably contains the two hydrazine ligands in a side-on bonding mode. The compounds were characterized by elemental analyses, IR, ^1H NMR and susceptibility measurements. The NH_2 protons are deshielded with respect to the free hydrazine by 3.8 to 5.6 ppm. For comparison, the complexes $VCl_3(amine)_x(thf)_y$ (amine = ethylenediamine, x and $y = 1$, **5**; tetramethylethylenediamine, $x = 2$, $y = 0$, **6**; *N*-aminopiperidine, $x = 1$, $y = 2$, **3**) have also been prepared.

Introduction

Metal bonded hydrazine is considered to be an intermediate in nitrogen fixation by primitive organisms such as *Azotobacter*, carrying a nitrogenase system. In *Azotobacter*, at least two nitrogenases, viz. a molybdenum and a vanadium nitrogenase are encoded [1]. The latter is expressed under molybdenum deficiency or in *nif*(HDK)$^-$ strains, i.e. in strains lacking the structural genes for the proteins of the Mo nitrogenase. The vanadium-based enzyme develops about 0.5% N_2H_4 per converted N_2 during catalytic turn-over [2]. Since N_2H_4 is not reduced by V nitrogenase, hydrazine cannot be a free intermediate, but is released directly from the enzyme system [2]. The related Mo enzyme does not form hydrazine in the process of *in vivo* N_2 fixation, but hydrazine has been detected after quenching of the enzyme with acid or alkali [3]. These facts, and the structural similarities between the two enzymes suggest a common mechanism for N_2 reduction.

The hydrazido(2−) species (M=N–NH_2) has been proposed as a source for both, ammonia and hydrazine, depending on whether N_α or N_β is protonated. Protonation of N_β, followed by further reduction, yields ammonia. Protonation of N_α leads to a hydrazido(1−) or hydrazinyl intermediate (M–NH–NH_2), which may evolve NH_3 (by disproportionation of the hydrazinyl radical) or N_2H_4 (by a second protonation step via {M–NH_2–NH_2}) [4]. Both products have been observed in the course of the reductive protonation of N_2 in the functional model compounds $[V(N_2)_2(diphos)_2]^-$ [4].

According to XANES data, the oxidation state of enzyme-bound vanadium lies between +II and +IV [5]. EPR measurements have shown that the reduced enzyme has a spin state of 3/2, with most of the spin density located on vanadium, hence V^{II} [6]. Hydrazine complexes of vanadium with the metal centre in these oxidation states are scarce, the only reported example being the V^{III} complex $[V(NH_2NHPh)_2salen]I$ [7]. On the other hand, several V^I ($CpV(CO)_3$hydrazine [8]) and V^{-I} complexes ($[V(CO)_5$hydrazine$]^-$ [9]) have been characterized. In all these complexes, end-on coordination prevails. Side-on coordination has been reported for the V^V complex $[VCl_2(NNMePh)(NH_2NMePh)]Cl$ [10], a compound which obviously contains two functional intermediates in N_2 fixation, viz. the hydrazine and hydrazido(2−) ligand. Recently, the dinuclear, N_2-bridged complex $[\{(o\text{-}Me_2NCH_2)C_6H_4\}_2V(py)]_2\mu\text{-}N_2$, formally with V^{II} if the bridging ligand is considered neutral, has been described [11] and shown to evolve NH_3 on treatment with HCl [12].

Experimental

General

All operations were carried out under N_2 atmosphere using standard Schlenk techniques. Solvents were dried and distilled under N_2 before use. Starting materials (1,2-bis(dimethylphosphino)ethane, dmpe; *N,N*-dime-

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thylhydrazine; ethylenediamine, en; *N,N,N',N'*-tetramethylethylenediamine, tmeda; *N*-aminopiperidine) were obtained from commercial sources (Strem, Merck). The following compounds were prepared according to the literature procedures: $VCl_3(thf)_3$ (**1**) [13]; tris(3-dimethylphosphinopropyl)phosphine, tdmp [14]. IR spectra were recorded on a Perkin-Elmer 1720 IFT spectrometer as KBr discs or in nujol mulls. ^1H NMR spectra were scanned on Bruker WP-80 or AM-360 spectrometers. Dry dmso-d_6 was used exclusively as solvent. All compounds were stable in dmso. Magnetic measurements for **2, 4** and **7** were performed at room temperature with a Johnson Matthey magnetic susceptibility balance. No susceptibility measurements were carried out for the other complexes, for which elemental analyses showed the presence of impurities.

$VCl_3\{NH_2N(CH_3)_2\}(C_4H_8O)_2$ (2)

60 mg (1.0 mmol) of a solution of *N,N*-dimethylhydrazine in 20 ml of thf were added to a solution of 0.65 g (1.74 mmol) of **1** in 20 ml of thf. The immediately generated, pink precipitate was filtered off after 12 h of stirring, washed with 20 ml of thf and 10 ml of pentane, and dried under vacuum. *Anal.* Calc. for $C_{10}H_{24}Cl_3N_2O_2V$ (361.62): C, 33.21; H, 6.69; N, 7.75; Cl, 29.41. Found: C, 34.03; H, 6.96; N, 6.98; Cl, 29.70%. Magnetic moment $\mu_{eff}=2.62$ BM ($\chi_{mol}\times10^{-6}=2747$).

$VCl_3(NH_2NC_5H_{10})(C_4H_8O)_2$ (3)

0.30 g (3.0 mmol) of *N*-aminopiperidine in 20 ml of thf was added dropwise to 1.12 g (3.0 mmol) of **1** in 50 ml of thf, where upon the colour of the reaction mixture turned from orange to violet. After 24 h of stirring, the solution was concentrated to 20 ml, resulting in the precipitation of a violet powder of **3**. This was filtered off, washed with 20 ml of cold thf and with 10 ml of pentane, and dried *in vacuo*.

$VCl_3(NH_2NMe_2)_2$ (4)

This complex was prepared from 0.21 g (3.52 mmol) of hydrazine and 0.33 g (0.88 mmol) of **1** in 20 ml of thf, following the procedure described for **2**. *Anal.* Calc. for $C_4H_{16}Cl_{13}N_4V$ (277.50): C, 17.31; H, 5.81; N, 20.19. Found: C, 18.29; H, 6.21; N, 20.80%. Magnetic moment $\mu_{eff}=2.65$ BM ($\chi_{mol}\times10^{-6}=2864$).

$VCl_3(H_2NCH_2CH_2NH_2)_2(C_4H_8O)$ (5) and $VCl_3\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}_2$ (6)

A solution of 0.38 g (1.02 mmol) of **1** in 10 ml of thf was treated portion-wise and with stirring with the ligand (equimolar amount in the case of **5**, molar ratio 1/1.6 in the case of **6**). The resulting violet solution was stirred for 24 h, the volume reduced to 5 ml, and the precipitate filtered off, washed with 10 ml of cold thf and 5 ml of pentane and dried under vacuum. The complexes were characterized by ^1H NMR and IR (cf. Tables 1 and 2).

$VCl_3\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}NH_2N(CH_3)_2\cdot0.5C_4H_8O$ (7)

0.27 g (1.79 mmol) dmpe was added to a solution of 0.67 g (1.79 mmol) of **1** in 10 ml of thf, whereupon the colour of the mixture turned from orange to dark green, indicating the formation of VCl_3(dmpe)thf. *N,N*-Dimethylhydrazine (0.1 g, 1.79 mmol) was added in three portions within 30 min. A violet precipitate formed, which was filtered off after 12 h of stirring, washed with 20 ml of thf and 20 ml of pentane and dried under vacuum. *Anal.* Calc. for $C_{10}H_{28}Cl_3N_2O_{0.5}P_2V$ (403.60): C, 29.76; H, 6.99; N, 6.99. Found: C, 29.59; H, 7.06; N, 7.05%. Magnetic moment $\mu_{eff}=2.61$ BM ($\chi_{mol}\times10^{-6}=2667$).

$VCl_3\{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2\}_2(C_4H_8O)$ (8)

1.0 g (2.7 mmol) of **1** and 1.25 g (3.1 mmol) of dppe were dissolved in 40 ml of toluene. A yellow precipitate formed within 48 h of stirring. The solid was filtered off, washed with 20 ml of toluene and 20 ml of pentane, and dried *in vacuo*. *Anal.* Calc. for $C_{30}H_{32}Cl_3OP_2V$ (627.83): C, 57.39; H, 5.14; Cl, 16.94. Found: C, 57.09; H, 5.01; Cl, 17.36%.

$VCl_2\{P[CH_2CH_2CH_2P(CH_3)_2]_3\}NH_2N(CH_3)_2$ (10) and $VCl_2\{P[CH_2CH_2CH_2P(CH_3)_2]\}$ (11)

0.25 g (0.67 mmol) of **1**, dissolved in 10 ml of thf, was treated with 0.23 g (0.67 mmol) of tdmp. To the green solution (containing VCl_3(tdmp)), a solution of lithium dimethylhydrazide was added, prepared from 0.04 g (0.67 mmol) NH_2NMe_2 dissolved in 4 ml of thf (-30 °C) and an equimolar amount of butyllithium in hexane. The reaction mixture was stirred at room temperature for 24 h. Treatment with 20 ml of pentane and cooling to 0 °C resulted in precipitation of violet **10**, which was filtered off, washed with 5 ml of pentane and dried *in vacuo*. The remaining filtrate was evaporated to dryness, the residue redissolved in pentane and cooled to -50 °C, whereupon blue **11** precipitated. The product was filtered off and dried *in vacuo*. *Anal.* Calc. for $C_{15}H_{36}Cl_2P_4V$: C, 38.98; H, 7.85; Cl, 15.34. Found: C, 38.75; H, 7.83; Cl, 15.18%.

Results and discussion

$VCl_3(thf)_3$ (**1**), which exhibits a *meridional* stereochemistry [15], reacts with H_2NNMe_2, when added slowly, to form pink $VCl_3(thf)_2(NH_2NMe_2)$ (**2a**). Vanadium is octahedrally coordinated. The hydrazine binds end-on through its NH_2 group, as shown by ^1H NMR (Table 1) and IR (Table 2) evidence.

TABLE 1. ^1H chemical shifts (δ/ppm) in the hydrazine region

Compound	H_2N–	–NMe_2
H_2NNMe_2	3.00	2.35
$VCl_3(NH_2NMe_2)(thf)_2$ (**2**)	8.57	2.70
$VCl_3(NH_2NC_5H_{10})(thf)_2$ (**3**)	7.98	
$VCl_3(NH_2NMe_2)_3$ (**4**)	6.83	*ca.* 2.51
VCl_3(en)thf (**5**)	8.43	
$VCl_3(tmeda)_2$ (**6**)		2.46
VCl_3(dmpe)NH_2NMe_2 (**7**)	7.79	2.61
VCl_2(tdmp)NH_2NMe_2 (**10**)	7.67	2.62

The ^1H NMR spectrum exhibits a resonance at 8.57 ppm, i.e. shifted to lower (magnetic) field by 5.5 ppm with respect to the free hydrazine, and broadened by quadrupole ($I(^{51}V)=7/2$, $Q=-0.04\times10^{-28}$ m^2) and paramagnetic relaxation. The downfield shift mainly reflects electron withdrawal from nitrogen upon coordination to vanadium. The Fermi contact shift by the paramagnetic V^{III} centre is negligible. The paramagnetism is reflected by $\mu_{eff}=2.62$ BM. The methyl protons give a slightly broadened, still structured signal, deshielded by 0.7 ppm relative to free H_2NNMe_2.

End-on coordination is further supported by a typical [16, 17] $\nu(NN)=924$ cm^{-1}. The $\delta(NH_2)$ vibration appears at 1610 cm^{-1}. Fast addition of hydrazine to a solution of **1** yields a compound with an additional $\delta(NH_2)=1560$ cm^{-1}. The most likely explanation is the formation of two isomers with the two thf ligands mutually *trans* (**2a**) or *cis* (**2b**), Scheme 1. A pink compound of composition $VCl_3(thf)_2$(N-aminopiperidine) (**3**), exhibiting spectroscopic properties very similar to **2a** (see Tables 1 and 2), has been obtained from the reaction between **1** and the hydrazine analogue aminoperidine.

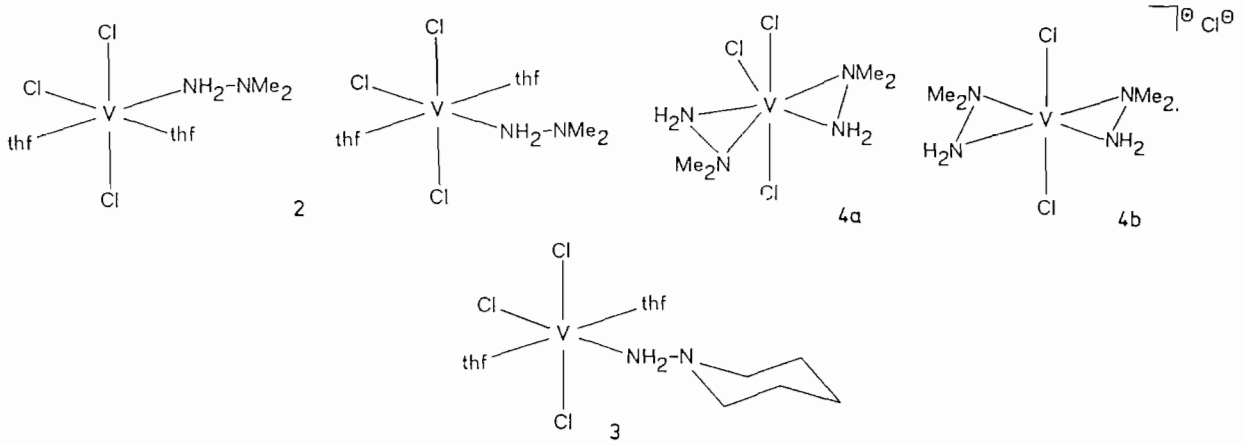
If an excess of H_2NNMe_2 is added to **1**, compound **4** is formed. One single $\nu(NN)=991$ cm^{-1} is observed, implying [18] a side-on coordination of both hydrazines. **4** may either be formulated as a seven-coordinate neutral complex (**4a** in Scheme 1) or as an ionic compound with an octahedrally coordinated vanadium centre (**4b**). The protons ($\delta=6.83$ ppm) are substantially less deshielded than in **2**, which is in accord with what one would expect if the two nitrogens coordinate.

In order to verify our assumption, based on NMR and IR data, that it is actually the NH_2 moiety of the hydrazine ligand which coordinates to the V^{III} centre, we have prepared the complexes VCl_3en(thf) (**5**) and $VCl_3(tmeda)_2$ (**6**) exclusively carrying ligated NH_2 and NMe_2, respectively. **5** shows a broad ^1H resonance at 8.43 ppm, which about coincides with that of **2**. Also, the IR pattern in the NH_2 region is similar to that of **2**. All vibrations in **5** are doubled, indicative of two geometric isomers. The complexation of tmeda clearly demonstrates that the NMe_2 function *can* coordinate. Shielding of the methyl protons does not differ from that in **2**, but the signal is significantly broadened by the near-by paramagnetic centre and therefore unstructured.

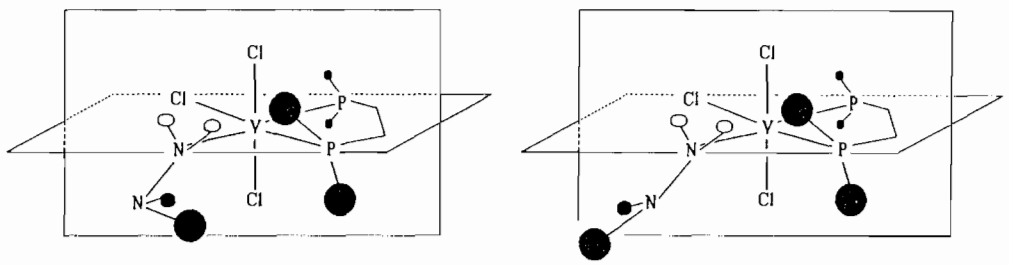
In the context of possible intermediates for the formation of NH_3 and N_2H_4 from the functional model $[V(N_2)_2(diphos)_2]^-$, we have also investigated the coordination properties of H_2NNMe_2 towards phosphine-stabilized V^{III}. Reaction of **1** with dmpe yields VCl_3(dmpe)thf [19]. Treatment of this compound with dimethylhydrazine in thf gives rise to the formation of violet VCl_3(dmpe)NH_2NMe_2 (**7**). Owing to the good electron donating properties of the phosphine ligand, the protons of the coordinating NH_2 are less deshielded in **7** (see Table 1) than in **2** and **5**. In the IR, the characteristic vibrations are again observed (Table 2). There is a set of two $\delta(NH_2)$ (1602 and 1589 cm^{-1}). Scheme 2 offers an explanation, based on the presence of two conformers. The reduced (with respect to phosphine-free **2**) electron donation of the hydrazine ligand leaves the coordinating N essentially sp^3 hybridized, the N–N bond a single bond, and the hydrazine in the *gauche* conformation. In this situation, an *endo* and an *exo* orientation of the NMe_2 moiety is possible.

TABLE 2. IR absorptions (cm^{-1}) in the hydrazine region

Compound	$\nu(NH_{as})$	$\nu(NH_s)$	$\delta(NH_2)$	$\nu(NN)$
H_2NNH_2	3348	3199	1600	940
$VCl_3(NH_2NMe_2)(thf)_2$ (**2**)	3296	3171	1610 (**2a**)	924
			1560 (**2b**)	
$VCl_3(NH_2NC_5H_{10})(thf)_2$ (**3**)	3247	3172	1608	920
$VCl_3(NH_2NMe_2)_2$ (**4**)	3246	3164	1577	991
			1561	
VCl_3(en)thf (**5**)	3297	3238	1581	
	3275	3219	1568	
VCl_3(dmpe)NH_2NMe_2 (**7**)	3208	3067	1602	938
			1589	
VCl_2(tdmp)(NH_2NMe_2) (**10**)	3368	3220	1592	943



Scheme 1.



Scheme 2.

Attempts to synthesize type **7** complexes with the phenylated dmpe analogue dppe failed. VCl_3(dppe)thf (**8**) prepared from $VCl_3(thf)_3$ and dppe, when reacted with H_2NNMe_2 in toluene, yields purely characterized products with a hydrazine/phosphine ratio of 3/2. In thf, **2** is formed, i.e. the phenylated phosphine, which is a much less powerful electron donor than the methylated one, is completely replaced by hydrazine.

The tripod phosphine tdmp reacts with **1** to form VCl_3tdmp (**9**) which is inert towards dimethylhydrazine. If, however, the lithium hydrazide $LiNHNMe_2$ is employed, reduction of V^{III} to V^{II} occurs and two compounds can be isolated, a cherry-red hydrazine complex of composition VCl_2(tdmp)(NH_2NMe_2) (**10**) and a blue hyrazine-free complex VCl_2tdmp (**11**), with the phosphine acting as a tetradentate ligand. With the exception of the presence of a resonance for NH_2, the ^1H NMR spectra of **10** and **11** are quite similar. ν(NN) = 938 cm^{-1} again supports an end-on coordination of the hydrazine.

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