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Model Studies of the Interaction of Vanadium(III) and Oxovanadium(IV/V) with the Carbonyl Amide Oxygen

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A series of vanadium(III) and oxovanadium(IV/V) compounds with the ligands, *N*-(2-nitrophenyl)pyridine-2-carboxamide (Hpycan), *N*-(phenyl)pyridine-2-carboxamide (Hpheca), and *N*-(2-pyridyl)acetamide (Hpyra), containing the amide functionality, was prepared and characterized both in solution and in solid state. All vanadium compounds contain a vanadium−amide oxygen bond. Crystal data for $[VOCl_2(OC_2H_5)(Hpheca)]$ (**4**) are monoclinic; $P2_1/a$; $a = 12.668(5)$ Å, $b = 8.084(3)$ Å, $c = 17.222(6)$ Å, $\alpha = 108.148(12)°$; $Z = 4$. In addition to the synthesis and crystallographic studies, the optical, infrared, and magnetic properties of these compounds are reported. Electron paramagnetic resonance [of oxovanadium(IV) species] and ^1H, $^{13}C\{^1H\}$, and ^{51}V nuclear magnetic resonance [of oxovanadium(V) compounds] properties are reported as well.

Introduction

The current explosive development in the coordination chemistry and biochemistry of vanadium,[2] is mainly due to the discovery that vanadium is an essential element in biological systems, participating in enzymic reactions such as bromination of a variety of organic substrates,[3] nitrogen fixation,[4] as well as to vanadium's insulinomimetic properties.[5] In addition, vanadate and oxovanadium(IV) species have shown great utility as tools in molecular biology for recognizing and understanding the binding sites and structure of proteins,[6] including phosphate binding proteins.[7] Recent X-ray crystallographic studies[8] of vanadium-containing proteins have indisputably demonstrated the binding of vanadium by the proteins.

These and many other biological implications of vanadium have made the exploration of interaction of vanadium with potential metal ion binding sites on proteins very important. The binding of a metal by a protein may principally involve ionazible side chains and the −NHCO− groups of the peptide chain backbone. The interaction of vanadium with the deprotonated amide (peptide) nitrogen has been well studied.[9,10] In marked contrast, there are only a very few structurally charac-

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terized examples and solution studies concerning the interaction of vanadium with the carbonyl oxygen of the −NHCO− functionality.[9h,11]

Herein we wish to report the synthesis, solid state, and solution properties of such vanadium compounds in oxidation states III, IV, and V. X-ray crystallography, magnetochemistry, and IR spectroscopy were used for the solid-state characterization, while UV/vis, NMR, and cw EPR[12] spectroscopy were used for characterization of the solution properties of these compounds. From this study it is evident that the amide carbonyl oxygen interacts with vanadium(III) and oxovanadium(IV/V).

Experimental Section

Materials. Reagent grade chemicals were obtained from Aldrich and used without further purification. Dichlorobis(tetrahydrofuran)-oxovanadium(IV), [VOCl$_2$(thf)$_2$],[13] trichlorooxovanadium(V), VOCl$_3$,[14] tris(acetonitrile)trichlorovanadium(III),

[VCl$_3$(CH$_3$CN)$_3$],[15] and *N*-(2-nitrophenyl)pyridine-2-carboxamide, Hpycan,[9b] were prepared by literature procedures. Merck silica gel 60 F254 TLC plates were used for thin-layer chromatography. Reagent grade dichloromethane, acetonitrile, and nitromethane were dried and distilled over powdered calcium hydride. Methyl alcohol, ethyl alcohol, and isopropyl alcohol were dried by refluxing over magnesium. Synthesis, distillations, crystallization of the vanadium compounds, and spectroscopic characterization, were performed under high-purity argon using standard Schlenk techniques. C, H, and N analyses were conducted by the University of Ioannina's microanalytical service, and vanadium and chloride were determined gravimetrically as vanadium pentoxide and silver chloride, respectively.

***N*-(Phenyl)pyridine-2-carboxamide (Hpheca).** Pyridine (10 mL) and triphenyl phosphite (2.96 g, 8.01 mmol) were added to a mixture of picolinic acid (2.20 g, 16.0 mmol) and aniline (1.51 g, 16.0 mmol). The mixture was refluxed overnight under magnetic stirring. The resulting solution was concentrated to 5 mL, and diethyl ether (50 mL) was slowly added under vigorous stirring. After the addition of diethyl ether was completed a slight precipitate was formed. The solution was kept at −25 °C overnight, and additional precipitate of off-white crystals was formed. The crystals were isolated by filtration, washed with *n*-hexane (2 × 5 mL) and dried in a vacuum. The isolated yield of Hpheca was 2.20 g (60%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 24 °C): δ (10.11, s, 1H), (8.66, d, 1H), (8.19, d, 1H), (7.99, q, 1H), (7.80, d, 2H), (7.58, t, 1H), (7.38, t, 2H), (7.14, t, 1H). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 24 °C): δ 161.93, 149.49, 147.81, 137.52, 129.34, 128.92, 126.33, 124.22, 122.21, 119.59, 115.37. Anal. Calcd for C$_{12}$H$_{10}$N$_2$O: C, 72.21; H, 5.08; N, 14.13. Found: C, 72.50; H, 5.01; N, 14.15. Mp: 64−65 °C. Mass spectrum (MS): *m*/*e* 198 [M]. R_f = 0.60 (4:1 chloroform/*n*-hexane).

***N*-(2-Pyridyl)acetamide Acetic Acid (Hpyra·CH$_3$COOH).** A solution of 2-aminopyridine (2.25 g, 24.0 mmol) in acetic anhydride (2.04 g, 20.0 mmol) was refluxed for 2 h. The resulting solution was evaporated to dryness to give an off-white solid which was recrystallized twice from hexane. The off-white crystals, from recrystallization, were isolated by filtration and dried under vacuum, yielding 3.64 g (85%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 24 °C): δ (12.7, s, 1H), (10.46, s, 1H), (8.31, d, 1H), (8.08, m, 1H), (7.74, m, 1H), (7.03, m, 1H), (2.19, s, 3H), (1.99, s, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 24 °C): δ 176.66, 169.67, 151.54, 145.06, 139.74, 119.18, 114.72, 24.14, 21.05. Anal. Calcd for C$_9$H$_{12}$N$_2$O$_3$: C, 56.09; H, 6.16; N, 14.28. Found: C, 54.84; H, 6.28; N, 14.27. Mp: 45 °C. MS: *m*/*e* 136 [M − CH$_3$COOH]. R_f = 0.25 (1:1 acetic ethyl ester/*n*-hexane).

***N*-(2-Pyridyl)Acetamide (Hpyra).** Non-recrystallized Hpyra·CH$_3$COOH (1.00 g, 5.10 mmol) was sublimed at 80 °C under high vacuum and over potassium hydroxide to obtain white crystals of Hpyra. The isolated yield was 0.35 g (50%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 24 °C): δ (9.32, s, 1H), (8.23, m, 2H), (7.69, m, 1H), (7.01, m, 1H), (2.17, s, 3H). ^{13}C{^{1}H} NMR (100.6 MHz, CD$_2$Cl$_2$, 24 °C): δ 168.86, 151.60, 147.12, 138.46, 119.47, 114.30, 24.32. Anal. Calcd for C$_7$H$_8$N$_2$O: C, 61.75; H, 5.92; N, 20.57. Found: C, 61.70; H, 5.85; N, 20.45. Mp: 63−64 °C. MS: *m*/*e* 136 [M]. R_f = 0.20 (1:1 acetic ethyl ester/*n*-hexane).

***mer*-Trichloro[*N*-(2-nitrophenyl)pyridine-2-carboxamide-N_p,O_{am}]-oxovanadium(V), [VOCl$_3$(Hpycan)] (1).** To a stirred solution of VOCl$_3$ (1.4 g, 8.1 mmol) in dichloromethane (10 mL) was slowly added Hpycan (2.11 g, 8.66 mmol) in dichloromethane (40 mL). Upon addition of Hpycan the orange color of the solution changed to deep red and a brick red precipitate was formed. The solid was filtered off, washed with cold dichloromethane (2 × 5 mL), and dried under vacuum, yielding 2.98 g (83%) of product. Anal. Calcd for C$_{12}$H$_9$Cl$_3$N$_3$O$_4$V: C, 34.60; H, 2.18; Cl, 25.53; N, 10.09; V, 12.23. Found: C, 34.57; H, 2.14; Cl, 25.50; N, 10.00; V, 12.15.

Acetonitrile-*cis*-dichloro[*N*-(2-nitrophenyl)pyridine-2-carboxamide-N_p,O_{am}]oxovanadium(IV), [VOCl$_2$(CH$_3$CN)(Hpycan)] (2). Method A. To a suspension of Hpycan (0.71 g, 2.9 mmol) in acetonitrile (20 mL) was slowly added under vigorous magnetic stirring a solution of [VOCl$_2$(thf)$_2$] (0.82 g, 2.9 mmol) in acetonitrile (20 mL). After 2 h of stirring at ambient temperature a light green precipitate was formed. The solid was filtered off, washed with diethyl ether (3 × 5 mL) and dried under vacuum, yielding 0.95 g (71%) of product. Anal. Calcd for C$_{14}$H$_{12}$Cl$_2$N$_4$O$_4$V: C, 39.84; H, 2.87; Cl, 16.80; N, 13.27; V, 12.07. Found: C, 40.09; H, 2.72; Cl, 16.83; N, 13.52; V, 12.21.

Method B. An alternative preparation for **2** is as follows: to a stirred solution of **1** (0.20 g, 0.48 mmol) in acetonitrile (15 mL) was added in one portion solid ferrocene (0.13 g, 0.72 mmol). After 2 h stirring the deep red color of the solution changed to light green and a green precipitate was formed. The solid was filtered off, washed with acetonitrile (2 × 5 mL) and dried under vacuum, yielding 0.13 g (67%) of product. This material showed identical properties to those of **2**.

(Acetonitrile)trichloro[*N*-(2-nitrophenyl)pyridine-2-carboxamide-N_p,O_{am}]vanadium(III), [VCl$_3$(CH$_3$CN)(Hpycan)] (3). To a suspension of Hpycan (0.396 g, 1.63 mmol) in acetonitrile (20 mL) was slowly added under vigorous stirring a solution of [VCl$_3$(CH$_3$CN)$_3$] (0.323 g, 1.63 mmol) in acetonitrile (10 mL). After 3 h stirring at ambient temperature, an olive green precipitate was formed. The product was filtered off, washed with diethyl ether (3 × 5 mL) and dried under vacuum, yielding 0.33 g (50%) of product. Anal. Calcd for C$_{14}$H$_{12}$Cl$_3$N$_4$O$_3$V: C, 38.08; H, 2.73; Cl, 24.08; N, 12.68; V, 11.53. Found: C, 38.01; H, 2.70; Cl, 24.12; N, 12.52; V, 11.38.

***trans*-Dichloro[*N*-(phenyl)pyridine-2-carboxamide-N_p,O_{am}]-*cis*-ethoxy-oxovanadium(V), [VOCl$_2$(C$_2$H$_5$O)(Hpheca)] (4). Method A.** To a stirred ethyl alcohol (3 mL) solution of VOCl$_3$ (0.2 g, 1 mmol) at −15 °C was added in one portion solid Hpheca (0.229 g, 1.15 mmol). Upon addition of the ligand a deep yellow precipitate was formed. The mixture was stirred for 0.5 h at −15 °C and additional 1 h at ambient temperature. The product was filtered off, washed with cold ethyl alcohol (2 × 4 mL) and dried under high vacuum for a week at 40 °C, yielding 0.32 g (82%) of product. Anal. Calcd for C$_{14}$H$_{15}$Cl$_2$N$_2$O$_3$V: C, 44.12; H, 3.97; Cl, 18.60; N, 7.35; V, 13.36. Found: C, 44.18; H, 3.94; Cl, 18.65; N, 7.39; V, 13.37.

Method B. An alternative preparation for **4** is as follows: To a stirred ethyl alcohol (6 mL) solution of VCl$_3$ (0.10 g, 0.64 mmol) was added in one portion solid Hpheca (0.13 g, 0.64 mmol). The color of the solution immediately changed from green to deep brown. Then, silver nitrate (0.22 g, 1.3 mmol) was added to it and the mixture was stirred for 7 h. Several color changes were ensued, followed by the formation

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(12) Abbreviations: cw EPR, continuous-wave electron paramagnetic resonance; NMR, nuclear magnetic resonance; COSY, correlated spectroscopy; NOESY, homonuclear Overhauser effect spectroscopy; ROESY, nuclear Overhauser effect spectroscopy in rotating frame; HMQC, heteronuclear multiple quantum coherence; HMBC, heteronuclear shift correlations via multiple bond connectivities.

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Table 1. Crystallographic Data for Complex **4**

empirical formula	$C_{14}H_{15}Cl_2N_2O_3V$
fw	381.13
temp, K	298
cryst system	monoclinic
space group	$P2_1/\alpha$
a, Å	12.668(5)
b, Å	8.084(3)
c, Å	17.222(6)
β, deg	108.148(12)
V, Å^3	1675.9(11)
Z	4
d_{calcd}/d_{measd} (g cm^{-1})	1.511/1.490
radiation; λ, Å	0.7107
abs coeff (μ), mm^{-1}	0.897
no. of data collcd/unique	3105/2954
no. of data used	2096[$Fo > 2.0\sigma(Fo)$]
R, R_w^{a,b}	0.0704, 0.1173

[a] $w = 1/[\sigma^2(F_o) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$ and $a = 0.0378$, $b = 1.1607$. [b] R based on F's, R_w based on F^2.

of a brown-orange solution and of a yellow precipitate. The solution was filtered off and by layering diethyl ether on the filtrate, orange, X-ray-quality crystals were precipitated. This material showed identical properties to those described for **4**.

***trans*-Dichloro[*N*-(phenyl)pyridine-2-carboxamide-N_p,O_{am}]-*cis*-methoxyoxovanadium(V), [VOCl$_2$(CH$_3$O)(Hpheca)] (5).** The molecule was prepared in a fashion similar to **4** (method **A**), except that methyl alcohol was used as a solvent. The isolated yield was 86%. Anal. Calcd for $C_{13}H_{13}Cl_2N_2O_3V$: C, 42.53; H, 3.57; Cl, 19.31; N, 7.63; V, 13.88. Found: C, 42.45; H, 3.52; Cl, 19.37; N, 7.58; V, 13.90.

***trans*-Dichloro[*N*-(phenyl)pyridine-2-carboxamide-N_p,O_{am}]-*cis*-isopropoxyoxovanadium(V), [VOCl$_2$(iC$_3$H$_7$O)(Hpheca)] (6).** The same procedure as for the above compound **4** (method **A**) was followed to prepare the complex, except that isopropyl alcohol was used as a solvent. The isolated yield was 79%. Anal. Calcd for $C_{15}H_{17}Cl_2N_2O_3V$: C, 45.59; H, 4.34; Cl, 17.94; N, 7.09; V, 12.89. Found: C, 45.63; H, 4.37; Cl, 17.91; N, 7.13; V, 12.83.

Bis{(μ_2-chloro)chloro[*N*-(phenyl)pyridine-2-carboxamide-N_p,O_{am}]oxovanadium(IV)}, [VO(μ_2-Cl)Cl(Hpheca)]$_2$ (7). The molecule was prepared in a fashion similar to **2** (method **A**). The isolated yield was 63%. Anal. Calcd for $C_{24}H_{20}Cl_4N_4O_4V_2$: C, 42.88; H, 3.00; Cl, 21.10; N, 8.33; V, 15.16. Found: C, 42.93; H, 3.08; Cl, 21.15; N, 8.34; V, 15.09.

(Acetonitrile)trichloro[*N*-(phenyl)pyridine-2-carboxamide-N_p,O_{am}]-vanadium(III), [VCl$_3$(CH$_3$CN)(Hpheca)] (8). The molecule was prepared in a fashion similar to **3**. The isolated yield was 65%. Anal. Calcd for $C_{14}H_{13}Cl_3N_3OV$: C, 42.40; H, 3.30; Cl, 26.82; N, 10.59; V, 12.85. Found: C, 42.38; H, 3.36; Cl, 26.79; N, 10.54; V, 12.82.

Bis{(μ_2-chloro)chloro[*N*-(2-pyridyl)acetamide-N_p,O_{am}]oxovanadium(IV)}, [VO(μ_2-Cl)Cl(Hpyra)]$_2$ (9). The molecule was prepared in a fashion similar to **2** (method **A**). The isolated yield was 55%. Anal. Calcd for $C_{14}H_{16}Cl_4N_4O_4V_2$: C, 30.68; H, 2.94; Cl, 25.88; N,10.22; V, 18.59. Found: C, 30.71; H, 2.91; Cl, 25.90; N, 10.19; V, 18.61.

(Acetonitrile)trichloro[*N*-(2-pyridyl)acetamide-N_p,O_{am}]vanadium(III), [VCl$_3$(CH$_3$CN)(Hpyra)] (10). The molecule was prepared in a fashion similar to **3**. The isolated yield was 71%. Anal. Calcd for $C_9H_{11}Cl_3N_2OV$: C, 32.32; H, 3.31; Cl, 31.79; N, 8.37; V, 15.23. Found: C, 32.40; H, 3.28; Cl, 31.81; N, 8.42; V, 15.27.

X-ray Structure Determination for Compound 4. Single crystals suitable for X-ray structure analysis were prepared as described in the preparation of the complex (method **B**). A crystal with approximate dimensions 0.10 × 0.30 × 0.30 mm was mounted in air and covered with epoxy glue. Intensity data were collected on a Crystal Logic dual goniometer diffractometer using graphite-monochromated Mo radiation. The unit cell constants (Table 1) were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11° < 2\theta < 23°$. Intensity data were recorded using a $\theta-2\theta$ scan to $2\theta_{max} = 50°$ with scan speed 3.0°/min and scan range 2.3 plus $\alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization correction was applied using Crystal Logic software. Symmetry equivalent data were averaged with $R = 0.0133$ to give 2954 independent reflections from a total 3105 collected. The structure was solved by direct methods using SHELXS-86[16] and refined by full-matrix least-squares techniques on F^2 with SHELXS-93[17] using 2954 reflections and refining 249 parameters. All hydrogen atoms [except those of C(14) which were introduced at calculated positions as riding on bonded atom] were located by difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically.

The final values for R, R_w, and GOF, for observed data are given in Table 1, for all data are 0.0426, 0.1013, and 1.033, respectively. The maximum and minimum residual peaks in the final difference map were 0.375 and −0.231 e/Å^3. The largest shift/esd in the final cycle was 0.038.

Physical Measurements. IR spectra were recorded on a Shimadsu FT-IR model 8601 in KBr pellets or Nujol. Electronic absorption spectra were measured as solutions in septum-sealed quartz cuvettes on a Perkin-Elmer Lamda 15 UV/vis spectrophotometer. Electron impact mass spectral data were obtained with a Kratos MS25RFA spectrometer. Melting points were determined (uncorrected) with a Buchi melting point apparatus. Magnetic moments were measured at room temperature by the Faraday method, with mercuric tetrathiocyanatocobaltate(II) as the susceptibility standard on a Cahn-Vetron RM-2 balance.

EPR Studies. Continuous-wave EPR spectra were recorded at liquid helium temperatures (20 K) with a Bruker ER 200 D X-band (9.42 GHz) spectrometer equipped with an Oxford Instruments Cryostat. The microwave frequency and the magnetic field were measured with a microwave frequency counter HP 5350B and a Bruker ER035M NMR gaussmeter, respectively. Care was taken to avoid line broadening due to overmodulation and power saturation. The experimental spectra were simulated by using the program SIMFONIA version 1.2 by Bruker, for an $S = {}^1/_2$ electron spin coupled to the $I = {}^7/_2$ nuclear spin from the ^{51}V nucleus.

Preparation of the NMR Samples. The solvents were dried over CaH$_2$ and distilled just prior use. All samples were prepared and measured in triplicate containing 5−10 mM complex (saturated solutions) under inert atmosphere using Schlenk techniques. The above precautions were not enough to avoid some decomposition of the complexes because of their low solubility and high sensitivity to hydrolytic decomposition and the insufficient dryness of the solvents for these experiments as shown by ^{1}H NMR spectroscopy.

NMR Studies. NMR spectra were recorded on a Bruker AMX 400 spectrometer at 223 to 263 K. Routine parameters were used when recording the ^{1}H and ^{13}C spectra. The chemical shifts are reported with respect to TMS as internal standard or to the resonance of the solvent.

The ^{51}V NMR spectra were recorded at 105 MHz, using a sweep width of about 50 000 Hz, a pulse angle of 90° and a relaxation time of 0.2 s. The ^{51}V NMR spectra were referenced to external VOCl$_3$. An exponential line broadening of 15 Hz or a Gaussian function (LB = −50, GB = 0.1) was imposed on the accumulated data before fourier transformation, at which point each ^{51}V NMR spectrum was phased; baseline corrected and integrated.

^{13}C NMR spectra were obtained at 100.6 MHz, and the assignment of the peaks was based on ^{1}H, ^{13}C HMQC, and HMBC experiments (gradient version). These spectra were acquired with 2K × 256 points, 32 and 128 scans per increment, respectively. The t_1 dimension was zero-filled to 1K real data points and 45° square sine-bell window functions were applied in both dimensions.

All 2D spectra were acquired at 300 K using TPPI method for quadrature detection except for 2D ^{1}H COSY which was recorded in magnitude mode. The 2D measurements were recorded using 256 increments of 2 K complex data points and 144 scans per increment for 2D ^{1}H NOESY or ROESY and 40 scans for 2D ^{1}H COSY experiments, respectively. The mixing time for NOESY spectra was 400 ms, and that for ROESY was 150 ms. 2D ^{1}H COSY were used for spin system assignment. Phase-sensitive 2D ^{1}H NOESY and ROESY

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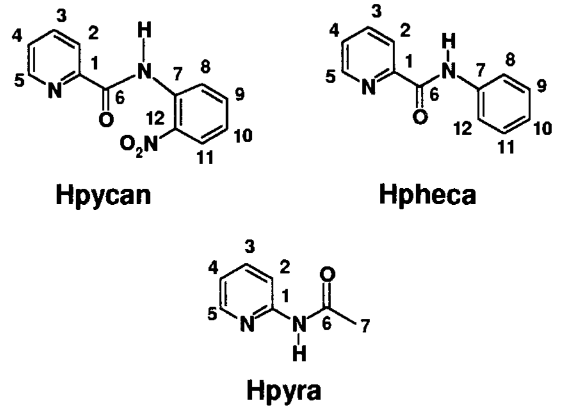
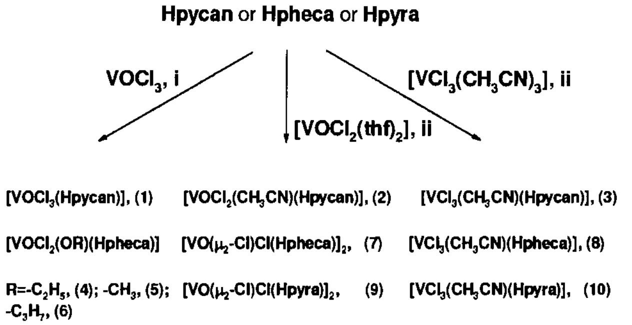
(16) Sheldrick, G. M. *SHELXS-86: Structure Solving Program*; University of Göttingen: Germany, 1986.

(17) Sheldrick, G. M. *SHELXS-93: Program for Crystal Structure Determination*; University of Cambridge: England, 1993.

Chart 1. Ligands Used in This Study



Scheme 1. Synthesis of the Oxovanadium(IV/V) and Vanadium(III) Compounds with the Ligands Hpycan, Hpheca, and Hpyra



i) Dicloromethane for **1**; ethyl alcohol, methyl alcohol and isopropyl alcohol for **4**, **5** and **6**. ii) acetonitrile

were used for specific assignment and chemical exchange observation. Data were processed by using UXNMR (Bruker) standard software. The t_1 dimension was zero-filled to 1 K real data points, and 0° or 45° phase-shifted sine bell window functions were applied in both dimensions for COSY and NOESY experiments, respectively.

Results and Discussion

Synthesis. The ligands used in this study are shown in Chart 1. The ligand Hpheca was prepared from picolinic acid and aniline in the presence of triphenyl phosphite and pyridine. Hpyra·CH_3COOH was prepared by condensing 2-aminopyridine with acetic anhydride. Hpyra·CH_3COOH had previously been prepared in a similar way, however the product of that synthesis had been identified as Hpyra and not as the 1:1 acetic acid derivative.[18] The acetic acid was removed by sublimation of Hpyra·CH_3COOH over potassium hydroxide to give Hpyra.

The vanadium(III) complexes **3**, **8**, and **10** were prepared by mixing [$VCl_3(CH_3CN)_3$] and Hpycan, Hpheca, and Hpyra in acetonitrile, respectively (Scheme 1). The organic ligands substitute two coordinated solvent molecules in the vanadium(III) precursor to form the desired compounds. These complexes are very unstable in solution and oxidized from the atmospheric oxygen forming their oxovanadium(IV) analogues **2**, **7**, and **9**, respectively. Even under inert atmosphere we were not able to prevent the oxidation of the vanadium(III) complexes, from small quantities of atmospheric oxygen that contaminated the solution.

The method of ligand substitution was also employed for the preparation of the $V^{IV}O^{2+}$ complexes **2**, **7**, and **9** (Scheme 1). [$VOCl_2(thf)_2$] was used as vanadium precursor. Complex **2** was also prepared by reduction of **1** with ferrocene in CH_3CN (eq 1).

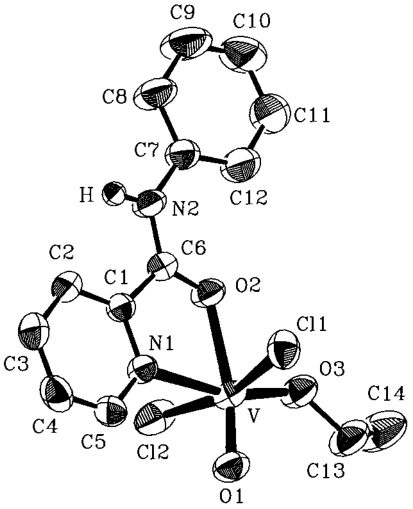


Figure 1. Molecular structure and numbering scheme for complex **4**.

$$\mathbf{1} + Fe(C_5H_5)_2 \rightarrow \mathbf{2} + Fe(C_5H_5)_2 + Cl^- \qquad (1)$$

These oxovanadium(IV) complexes are water sensitive in solution and solid state. In the solid state, they are readily hydrolyzed from the humidity of the atmosphere in less than an hour, but they are stable for weeks under inert atmosphere.

The vanadium(V) complex **1**, was prepared by addition of Hpycan to a dichloromethane solution of $VOCl_3$. Similar method was employed for the preparation of the complexes **4**−**6** with the ligand Hpheca, except that methyl alcohol, ethyl alcohol or isopropyl alcohol were used as solvents respectively instead of dichloromethane (Scheme 1). In these complexes one of the chlorine ligands was replaced with an alkoxy group (eq 2).

$$VOCl_3 + Hpheca + HOC_2H_5 \rightarrow \mathbf{4} + HCl \qquad (2)$$

Complex **4** was also prepared by oxidation of the reaction mixture of vanadium(III) and Hpheca, with $AgNO_3$ and oxygen in ethyl alcohol. Complex **1** is water sensitive and is stable in solution and solid state only under inert atmosphere. Complexes **4**−**6** are also water sensitive but they are more stable than **1**. For example, complexes **4**−**6** are stable in solid state for more than 1 day without protection, in contrast to **1**, that is decomposed almost immediately after exposure to air.

X-ray Crystal Structure of 4. Figure 1 shows the structure and the labeling scheme of complex **4** as characterized by X-ray crystallography. A selection of interatomic distances and bond angles relevant to the vanadium coordination sphere in **4** is listed in Table 2. The vanadium atom has a distorted octahedral geometry. It is bonded to a bidentate Hphepca ligand at the pyridine nitrogen atom [N(1)] and the O_{amide} atom O(2), as well as an oxo O(1) and an ethoxy [O(3)] groups and two chlorine atoms Cl(1) and Cl(2) and is 0.24 Å above the mean equatorial plane (mean deviation 0.03 Å) [defined by N(1), O(3), Cl(1), and Cl(2)] in the direction of the oxo ligand. The amide functionality C(1)−C(6)−O(2)−N(2) is planar within the limits of precision.

The carbonyl oxygen atom of the amide group in complex **4** is coordinated trans to the oxo ligand, as also observed in four structurally characterized oxovanadium(IV/V) compounds, with a V−O_{amide} bond.[9h,11a−c] There is a sixth known structure

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[18] Nonoyama, M.; Tomita, S.; Yamasaki, K. *Inorg. Chem. Acta* **1975**, *12*, 33.

Table 2. Interatomic Distances (Å) and Angles (deg) Relevant to the Vanadium Coordination Sphere for **4**

V−O(1)	1.585(3)	V−N(1)	2.203(3)
V−O(3)	1.746(3)	V−Cl(2)	2.325(2)
V−O(2)	2.184(2)	V−Cl(1)	2.356(2)
O(1)−V−O(3)	103.01(13)	O(2)−V−Cl(2)	84.88(8)
O(1)−V−O(2)	165.65(12)	N(1)−V−Cl(2)	83.98(8)
O(3)−V−O(2)	91.26(11)	O(1)−V−Cl(1)	94.52(11)
O(1)−V−N(1)	93.09(13)	O(3)−V−Cl(1)	93.76(10)
O(3)−V−N(1)	163.73(11)	O(2)−V−Cl(1)	82.84(8)
O(2)−V−N(1)	72.60(10)	N(1)−V−Cl(1)	82.47(8)
O(1)−V−Cl(2)	94.82(11)	Cl(2)−V−Cl(1)	163.92(5)
O(3)−V−Cl(2)	96.85(10)		

containing the unit *cis*-$V(=O)(O_{amide})$, but in this case the cis configuration is imposed by the tripodal ligand *N*-(carbamoylmethyl)iminodiacetic acid (H_2ada).[11d] The V^{v}-O_{amide} bond length [2.184(2) Å] is the shortest so far reported in a compound containing the unit *trans*-$V^{IV/V}(=O)(O_{amide})$. The mean $V^{IV/V}$-O_{amide} bond distance for oxovanadium(IV/V) compounds with the unit *trans*-$V(=O)(O_{amide})$ is ~2.2 Å, but only ~2.0 Å in the cis case.

From the data of Table 3, it is evident, for the compounds **1**, **2**, and $[VO(NH_2O)_2(glygly)]$, containing the unit *trans*-$V^{IV/V}(=O)(O_{amide})$, that the $V-O_{amide}$ bond length is reduced as the V=O bond length is increased and this is reasonable. Compounds **4** and $[VOCl(Hbpb)]_2{\cdot}2CH_3NO_2$ {H_2bpb = 1,2-bis(2-pyridinecarboxamide)benzene} do not follow this trend. For **4**, this might be due to the absence of the $-NO_2$ substituent on the aromatic ring, which is present in **1** and **2**, and influences the >C=O bond length as a result of inductive effects, while for $[VOCl(Hbpb)]_2{\cdot}2CH_3NO_2$ its dimeric character might be responsible for it.

The V=O bond length [1.585(3) Å] of **4** is very similar to those previously reported for octahedral oxovanadium(V) compounds.[11a,19] The V−O(3) bond distance [1.745(3) Å] is also consistent with values found in other oxovanadium(V) alkoxide compounds.[20] The VCl_2 group is in the trans configuration with the Cl(1)−V−Cl(2) angle of 163.93(5)° and V−Cl(1) and V−Cl(2) distances of 2.356(2) and 2.325(2) Å, respectively. Two types of weak hydrogen bonding between the Cl(1) and HN′(2) of a second molecule and the Cl(2) and the HN″(2) of a third molecule in **4** are observed [N′(2)−Cl(1) = 3.468(3) Å, N″(2)−Cl(2) = 3.558(3) Å]. This interaction is probably responsible for the 0.032(2) Å elongation of the V−Cl(1) bond length compared to V−Cl(2).

A comparison of the structures of compounds **4**, **1**[11a] (Figure 2), and **2**[11a] (Figure 3) reveals that the molecules are very similar (Table 3). Namely, (i) the $V-N_{pyridine}$ bond length in **1** and **2** is identical [2.16 Å] within experimental error while in **4** is a bit longer [2.20 Å] as a consequence of the trans influence of the ethoxy group, and (ii) the V=O and mean V−Cl bond lengths are almost identical in **2** and **4** (Table 3) and shorter in **1**. This difference between **1** and **4** is probably due to the coordination of the ethoxy ligand in **4** and between **1** and **2** is presumably due to lower oxidation state in **2**.

Magnetism and Electron Paramagnetic Spectra. The complexes **1** and **4**−**6** are diamagnetic as expected for a d^0 system, while the vanadium(III) complexes **3**, **8**, and **10** have magnetic moments of 2.87, 2.52, and 2.50 μ_B respectively in accord with the expected value for a d^2 system. Complexes **7** and **9** have magnetic moments of 1.22 and 1.18 μ_B respectively which are lower than the expected value for a d^1 system, observed for the monomeric oxovanadium(IV) complex **2** (1.74 μ_B). These magnetic moments reveal that complexes **7** and **9** have higher nuclearities and there are d^1−d^1 electron interactions between the vanadium(IV) nuclei. Additional information of the structure of these complexes in the solid state was obtained from IR spectroscopy as described below.

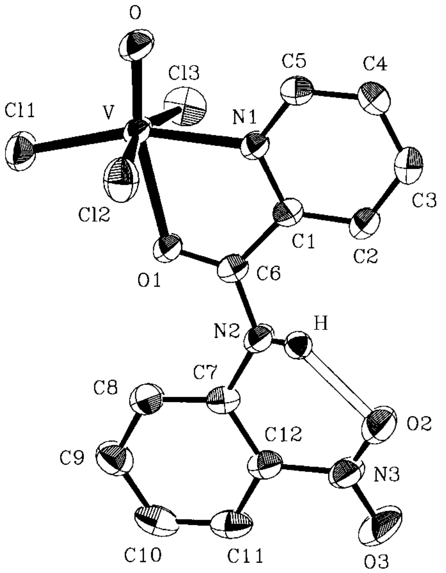

Figure 2. Molecular structure and numbering scheme for complex **1** (from ref 11a).

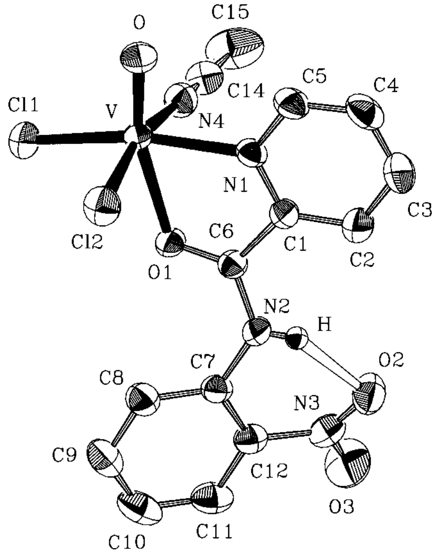

Figure 3. Molecular structure and numbering scheme for complex **2** (from ref 11a).

The EPR parameters (from anisotropic spectra) for the oxovanadium(IV) complexes **2**, **7**, and **9** are listed in Table 4. A progressive decrease of the g_z value with a concomitant increase of the A_z value is observed on going from Hpheca to Hpycan and then to Hpyra. The A_z value of **9** does not follow this trend. The EPR data show that in solution (acetonitrile) compounds **2**, **7**, and **9** exist as mononuclear species. The EPR parameters g_z and A_z were found to be solvent dependent, indicating that the coordination environment of these three complexes is sensitive to the solvent type.

NMR Studies. The ^{51}V NMR spectrum of **1** gave one resonance at −95 ppm in CD_2Cl_2 and three resonances at +19,

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(19) Cornman, C. R.; Kampf, J.; Pecoraro. V. L. *Inorg. Chem.* **1992**, *31*, 1983.

(20) (a) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1990**, *24*, 3013. (b) Crans D. C.; Chen H.; Anderson, O. P.; Miller, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 6769.

Table 3. Comparison of Various Bond Lengths, for All Oxovanadium(IV/V) and Vanadium(III) Compounds Structurally Characterized and Containing a $V-O_{Amide}$ Bond

compound	$V-O_{amide}$	V═O	V−Cl[a]	$V-N_{pyridine}$	oxidation state	ref
1	2.214(1)	1.572(1)	2.252(1)	2.160(2)	V	11a
2	2.206(1)	1.587(1)	2.336(1)	2.162(2)	IV	11a
4	2.184(2)	1.585(3)	2.341(2)	2.203(3)	V	this work
$[VO(NH_2O)_2(glygly)]$	2.188(3)	1.614(3)	−	−	V	11b,c
$[VO(ada)(H_2O)]$	2.012(2)[b]	1.601(2)	−	−	IV	11d
$[VOCl(Hbpb)]_2{\cdot}2CH_3NO_2$	2.217(2)	1.587(2)	2.355	2.13(2)	IV	9h
$[V(Hbpb)_3]{\cdot}2CHCl_3$	1.955(3)[c,d]			2.139(4)	III	9h

[a] Mean value of all V−Cl bonds for each vanadium compound. [b] The $V-O_{amide}$ bond is cis to the oxo group, in contrast to all other cases reported in this table, where the $V-O_{amide}$ bond is trans to O^{2-}. [c] Mean value of the two $V-O_{amide}$ bonds. [d] The $V^{III}-O_{amide}$ bond length of 1.955 Å is indicative of a strong interaction, but in this case, in contrast to the general trend, the O_{amide} atom is ligated to vanadium instead of the deprotonated amide nitrogen of the $-CON^{-}-$functionality.

Table 4. EPR Parameters for the Oxovanadium(IV) Complexes **2**, **7**, and **9** in Frozen Acetonitrile Solutions (77 K)

				A, cm^{-1} × 10^{-4}		
complex	g_x	g_y	g_z	A_x	A_y	A_z
2	1.970	1.980	1.940	66.00	65.00	175.0
7	1.970	1.966	1.949	55.00	55.00	166.0
9	1.970	1.980	1.931	66.00	65.00	171.0

Table 5. ^1H and ^{13}C NMR Chemical Shifts (ppm) and the CIS (ppm) Values of Hpycan and Complex **1** in CD_2Cl_2 Solution; Numbering of the Protons and Carbons Is as In Chart 1

	Hpycan		**1**		CIS = $\delta_{BOUND} - \delta_{FREE}$	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
NH	12.70	−	12.47	−	−0.23	−
1	−	150.34	−	145.51	−	−4.8
2	8.28	123.84	8.28	125.14	0.00	1.3
3	7.97	139.04	8.38	143.50	0.41	4.5
4	7.58	128.38	7.96	132.08	0.38	3.7
5	8.74	149.78	9.31	154.20	0.57	4.4
6	−	164.43	−	164.97	−	0.5
7	−	138.00	−	138.53	−	0.5
8	8.26	127.10	8.42	127.78	0.16	0.7
9	7.25	124.55	7.55	128.29	0.30	3.7
10	7.74	137.06	7.99	138.65	0.25	1.6
11	9.01	122.96	9.08	124.28	0.07	1.3
12	−	135.72	−	132.69	−	−3.0

Table 6. ^1H and ^{13}C NMR Chemical Shifts (ppm) of Hpycan and Vanadium(V) Species of Complex **1** in CD_3CN Solution; Numbering of the Protons and Carbons Is as in Chart 1

	Hpycan		**1a**		**1b**	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
NH	12.66	−	10.90	−	11.21	−
1	−	150.23	−	141.72	−	144.43
2	8.24	123.28	8.56	125.64	8.41	125.98
3	8.03	139.05	8.84	149.87	8.44	144.07
4	7.64	128.28	8.28	131.34	7.99	132.21
5	8.73	149.46	8.88	143.87	9.24	153.51
6	−	163.69	−	157.49	−	165.53
7	−	138.17	−	140.94	−	142.00
8	8.26	126.73	8.22	126.81	8.28	127.03
9	7.29	124.29	7.50	127.51	7.62	129.15
10	7.78	136.68	7.84	136.38	7.93	136.38
11	8.97	122.29	8.24	124.98	8.30	126.51
12	−	135.05	−	131.22	−	129.64

−96, and −366 ppm in CD_3CN at 238 K. The NMR spectra of **1** were acquired at low temperature, because the complex was more stable to reduction at lower temperatures.

^1H and ^{13}C NMR spectroscopy is a powerful tool in deciphering the solution structure of vanadium(V) species observed from ^{51}V NMR spectroscopy.[21] The full assignment of the proton and carbon atoms of the free ligand (Hpycan) and its oxovanadium(V) complex, as well as the coordination-induced shift (CIS) values, in CD_2Cl_2, are reported in Table 5. The CIS value for a given nucleus is defined as the difference between its chemical shift in the complex versus that in the free ligand, CIS = $\delta_{bound} - \delta_{free}$. The assignments were based on COSY and NOESY experiments. The chemical shifts of C(1) and C(5) in the complex show significant shift from those of the free ligand, with CIS values −4.8 and 4.4 ppm, respectively. These shifts are consistent with the pyridine nitrogen ligation to vanadium atom in a position cis to the oxo group.[22] The small shift, CIS = 0.5 ppm, observed for C(6) (the carbonyl carbon) is possibly due to an equilibrium between a species, where the carbonyl oxygen of the −NHCO− group is coordinated to vanadium and a species where the carbonyl oxygen is not coordinated, with the latter being the predominant one. From these data, it is concluded that the solution structure of **1** in CD_2Cl_2 is similar to that found in the crystal structure, where the vanadium atom has an octahedral geometry and it is bonded to an amide oxygen, (trans to the O^{2-}), to an oxo group as well as to a pyridine nitrogen and three chlorines in meridional position[11a] (Figure 2).

The interpretation of the NMR spectra of **1** in CD_3CN is more complicated due to its low solubility and the hydrolysis of it. ^1H and ^{13}C NMR spectra of **1** in CD_3CN showed two sets of aromatic protons and carbons, one of a ligand coordinated to vanadium and the other of a ligand noncoordinated to vanadium (Table 6). Figure 4 shows the ^1H NMR spectra of **1** in CD_2Cl_2 and CD_3CN. The peaks of the non coordinated ligand in ^1H and ^{13}C NMR spectra were identified with addition of a small quantity of Hpycan in CD_3CN solution of **1**.

The chemical shift of the peak at −96 ppm (**1b**) of **1** in CD_3CN solution in ^{51}V NMR spectrum is similar to the chemical shift of the peak observed for **1** in CD_2Cl_2 solution (−95 ppm) and thus it is assigned to the same vanadium species. The ^{13}C NMR CIS values observed for the coordinated ligand to vanadium in CD_2Cl_2 are very close to those observed for **1b** in CD_3CN suggesting similar coordination of the ligand to vanadium in both solvents (Tables 5 and 6). The strong coordination of the pyridine nitrogen atom to vanadium, in addition to the above-mentioned reasoning (CD_2Cl_2 solvent), is also proved from the differences in the ^3J values of the H(4) and H(5) between the free Hpycan and the Hpycan coordinated to vanadium. In CD_2Cl_2 or in CD_3CN solutions the $^3J_{4,5}$ of the free ligand is 4.64 Hz and that of the complex is 5.60 Hz suggesting reduction of the pyridine nitrogen electronic density.

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(21) (a) Crans, D. C.; Shin, P. K. *Inorg. Chem.* **1994**, *33*, 1305. (b) Crans, D. C.; Shin, P. K.; Armstrong, K. B. In *Mechanistic Bioinorganic Chemistry*; Thorp, H., Pecoraro, V., Eds.; American Chemical Society: Washington, DC, 1995; p 303.

(22) Crans, D. C.; Keramidas, A. D.; Amin, S. S.; Anderson, O. P.; Miller, S. M. *J. Chem Soc., Dalton Trans.* **1997**, 2799.

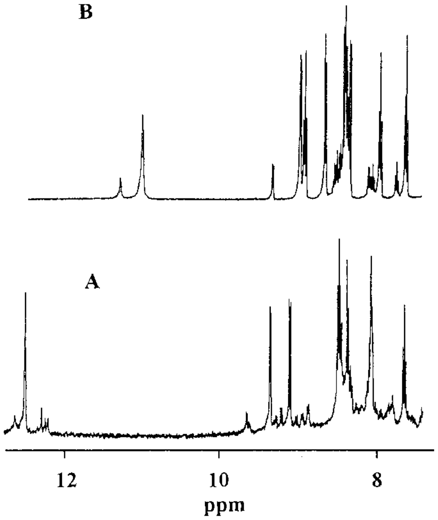

Figure 4. ^{1}H NMR spectra of **1** in CD_2Cl_2 (A) and in CD_3CN (B). A 90° pulse was used in all cases; the repeatition rate was 0.1 s^{-1} and the Gaussian multiplication was used for the processing of the FIDs. The spectra were recorded at 238 K.

Comparison of the integrals of the peaks in ^{1}H NMR spectrum of the coordinated and free ligand with the peaks of the ^{51}V NMR spectrum in CD_3CN, shows that the peaks at +19 and −366 ppm are from species with no ligand coordinated to vanadium atom. The peak at +19 ppm is assigned to $[VOCl_4]^-$ species,[23,24,25b] while the peak at −366 ppm is probably a hydrolysis product $[VO_2Cl_2]^-$.[24]

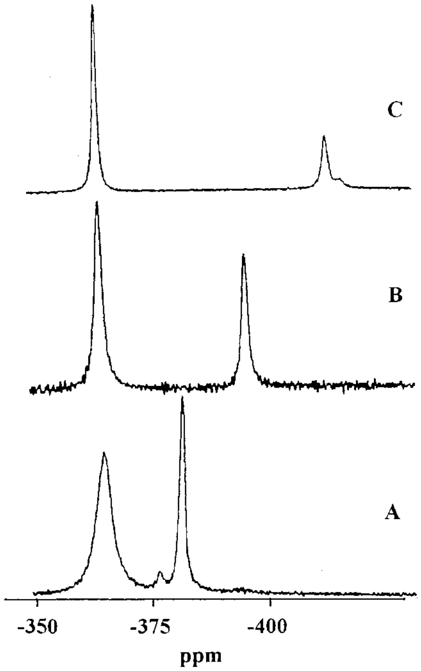

Figure 5. ^{51}V NMR spectra of **5** (A), **4** (B), and **6** (C) in CD_3CN. A 90° pulse was used in all cases, the repeatition rate was 10 s^{-1} and the same Gaussian multiplication was used for all processing of the FIDs. The spectra were recorded at room temperature.

Table 7. ^{1}H NMR Chemical Shifts (ppm) of Hpheca and the Vanadium(V) Species of Complexes **4**−**6** in CD_3CN Solution; The Numbering of the Protons Is as in Chart 1

		4		**5**			**6**	
	Hpheca	**a**	**b**	**a**	**b**	**c**	**a**	**b**
NH	10.11	9.69	9.81	9.66	9.93	10.15	9.60	9.79
H(2)	8.19	8.59	8.41	8.60	9.42	–	8.58	8.39
H(3)	7.99	8.69	8.29	8.78	8.36	8.30	8.69	8.34
H(4)	7.58	8.16	7.92	8.21	7.93	7.86	8.16	7.92
H(5)	8.66	8.83	9.38	8.83	9.37	9.07	8.84	9.39
H(8),(12)	7.80	7.77	7.71	7.77	7.70	–	7.76	7.72
H(9),(11)	7.38	7.47	7.51	7.46	7.51	7.53	7.46	7.51
H(10)	7.14	7.28	7.36	7.28	7.36	7.42	7.28	7.36
H(13)	–	3.53	6.00	3.24	5.62	5.93	3.86	6.60
H(14)	–	1.11	1.54	–	–	–	1.08	1.54

The ^{51}V NMR spectra of the alcoxy complexes **4**−**6** in CD_3CN and CD_3NO_2 are considerably different from the spectra of **1** despite of the similarity between the amide ligands Hpheca and Hpycan (Chart 1). These spectra gave two major resonances at −365 (**4a**) and −397 ppm (**4b**) for **4**, at −365 (**5a**) and −381 ppm (**5b**) for **5**, and at −365 (**6a**) and −412 ppm (**6b**) for **6** (Figure 5). Minor peaks were also observed at −377 (**5c**) and −417 ppm (**6c**) for **5** and **6** respectively (Figure 5). The ^{51}V NMR spectrum of **4** in CD_3CN did not show any peak from a minor complex while its ^{1}H NMR spectrum showed that there are three species in solution and one of these is from a minor species similar to those observed for **5** and **6**. The peak of **4c** in ^{51}V NMR spectrum of **4** is probably very close or under the absorption of the major species **4b**. The ^{51}V NMR chemical shifts of the peaks are identical in both solvents, CD_3CN and CD_3NO_2, indicating that the solvent did not participate in the coordination sphere of vanadium. The ^{51}V NMR chemical shifts of the peaks of the vanadium(V) alcoxy complexes, such as $[VOCl_2(OCH_3)]$ (−290 ppm), $[VOCl_2(OC_2H_5)]$ (−300 ppm), and $[VOCl_2(O\text{-}i\text{-}C_3H_7)]$ (−309 ppm), are sensitive to the type of the alcoxide coordinated to the vanadium atom.[25] The ^{51}V NMR spectra of **4**−**6**, in addition to the other ^{51}V signals, gave also a peak at −365 ppm for all complexes (vide supra). Apparently this signal at −365 ppm for complexes **4**−**6** comes from a vanadium(V) species that does not contain an alcoxy group ligated to vanadium. The rest of the peaks show the expected shifting for vanadium coordinated with one alcoxy group (CH_3O^-, $C_2H_5O^-$, and $iC_3H_7O^-$). Furthermore ^{51}V NMR spectroscopy showed that addition of methyl alcohol in an CD_3CN solution of **5** changed the equilibrium toward to the peak at −381 ppm, supporting the previous assumption. For example, addition of six equivalents of methanol into an acetonitrile solution of **5** changed the molar ratio of the three vanadium(V) species, **5a**, **5b**, and **5c**, from 1.9, 1.0, and 0.15 to 0.72, 1.0, and 0.10, respectively.

Due to the low solubility of complexes **4**−**6** ^{13}C NMR analysis was not carried out. ^{1}H NMR spectroscopy was used to decipher the solution structure of vanadium(V) species observed from ^{51}V NMR spectroscopy. The chemical shifts and the assignments of the ^{1}H NMR spectra for complexes **4**−**6** in CD_3CN are summarized in Table 7 and shown in Figure 6. The assignments were based on COSY and NOESY experiments. The ^{1}H NMR spectra of **4**−**6** in CD_3CN showed signals from three different spin systems in the aliphatic region, two major and one minor. One of these belongs to free ROH (where R = CH_3^- or $C_2H_5^-$ or $iC_3H_7^-$) and this was confirmed from the ^{1}H NMR spectra of the CD_3CN solution of **4**−**6** with addition of a small quantity of ROH. The other two, one major and one minor, belong to an alcoxy group bound to vanadium**.** The positive part of the NOESY spectrum of **4** (Figure 7) which contains the exchange peaks, shows that there is a slow exchange at the NMR time scale between these three spin systems. The

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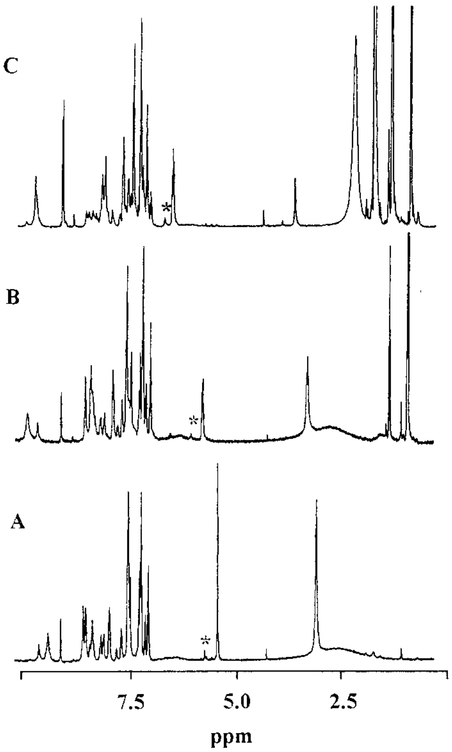


Figure 6. ^{1}H NMR spectra of **5** (A), **4** (B), and **6** (C) in CD_3CN. 90° pulse was used in all cases, the repeatation rate was 0.1 s^{-1} and the Gaussian multiplication was used for the processing of the FIDs. The asterisks (*) denote the minor conformer. The spectra were recorded at room temperature.

lability of the ethoxy group shown in this spectrum is in agreement with the lability observed for other vanadium alkoxy compounds.[21,22]

The same pattern was observed in the aromatic region. The 1D ^{1}H NMR spectra of **4**−**6** show all the signals from the two major forms and a few from the minor form. The absence of some of the signals of the minor form is due to the complexity of the spectra in this region and its low concentration (less than 2% of the total vanadium). In the NOESY spectrum of **4**, there are all the exchange peaks in the aromatic region, between the peaks of the major forms and between the major forms and the minor form. A detailed analysis of complex **5**, the compound with the highest solubility, using ^{1}H−COSY NMR permitted the full assignment of all the resonances from the three species in solution (Table 7). A comparison of the results with those from free Hpheca leads to the conclusion that the ligand is bound to vanadium in all three species. This is also supported by ^{51}V and ^{1}H NMR variable temperature experiments**.** In these experiments the ratio of **5a** and **5b** changed from 4 and 1 at 298 K to 0.7 and 1 at 238 K, respectively.

The chemical shifts of the pyridine ring protons of the bound ligand, show significant shift from those of the free ligand suggesting a strong coordination of the pyridine nitrogen. The difference of the chemical shifts of the amide hydrogen between the bound and the free Hpheca (CIS ≈ -0.2 ppm for the alcoxy complex and CIS ≈ -0.4 ppm for the alkoxy free complex) in complexes **4**−**6**, are in the range of the shift observed for complex **1** (CIS $= -0.15$ ppm). ^{1}H NMR spectroscopy supports that Hpheca, in the three species generated after dissolution of **4**−**6** is coordinated in a way similar to that found in the crystal structure of **4**. The pyridine nitrogen is coordinated in a position cis to the oxo group and the amide oxygen in a position trans to the oxo group.

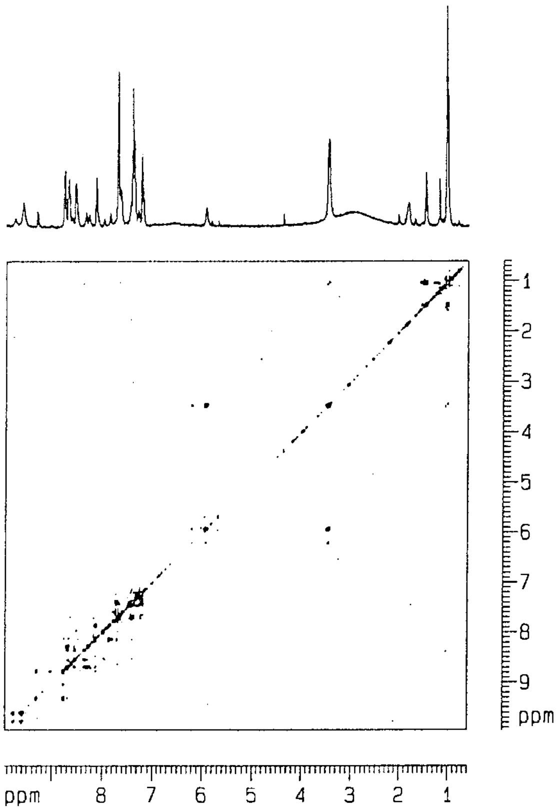


Figure 7. 2D ^{1}H-NOESY spectra of compound **4** in CD_3CN. The spectra were recorded at room temperature, using 256 increments of 2 K complex data points and 144 scans per increment and mixing time of 400 ms.

The quantity of the two species (**a**, **b**) in saturated CD_3CN solutions of compounds **4**−**6** containing various concentrations of water was measured by integration of their ^{51}V NMR signals and it was found that increasing the quantity of water in solution the species at −365 ppm was also increased. In addition, running the ^{51}V NMR spectra of **4**−**6** in CD_2Cl_2, which solvent is not hydrophilic like CD_3CN, only a very small quantity of the species at −365 ppm was detected. At high water concentrations both complexes were decomposed completely to give other vanadium species**.** From these experiments it is concluded that the peak at −365 ppm is a hydrolytic product. At this point, it is worth noting that the amide ligand remains coordinated to vanadium in all complexes, thus showing higher stability to hydrolysis than the alkoxy group. The alkoxy group is a strong base and probably accepts the protons from the hydrolysis of **4**−**6**, protecting the coordination of the amide ligand to vanadium. It is reasonable to assume that the water competes with the alcoxy group for the binding site in the complex.

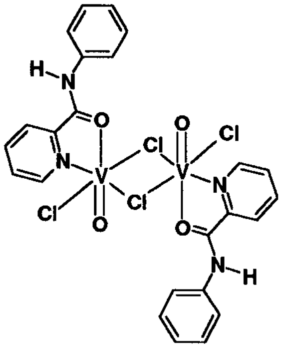
Infrared Spectroscopy. Assignments of some characteristic infrared bands are given in Table 8. The ν(N−H) bands are present in the spectra of all the vanadium compounds, as expected from the stoichiometry. The strong ν(C═O) peaks are about 40 cm^{-1} lower in the complexes compared to the peaks of the free ligands. This change is to be expected as a result of the coordination of the carbonyl amide oxygen to vanadium. All oxovanadium(IV/V) complexes show a strong ν(V═O) band at $\approx$980 cm^{-1}. The ν(V−Cl) bands appear between 315 and 410 cm^{-1}. These bands are single strong peaks except in **1**, **7**, and **9** which gave two peaks. **1** is expected to have two peaks as a mer isomer. The far-IR spectra of complexes **7** and **9** are indicative of both terminal and bridging V−Cl bonds. The strong bands at 360 and 355 cm^{-1} of **7** and **9**, respectively, arise from

Table 8. Characteristic Infrared Bands (cm^{-1}) of the Ligands and Their Vanadium Complexes

	infrared bonds			
compounds	ν(N−H)	ν(C=O)	ν(V=O)	ν(V−Cl)
Hpycan	3283 m	1698 s		
1	3231 m	1605 s	984 s	410 s, 354 s
2[a]	3321 m	1662 s	982 s	354 s
3[b−d]	3160 m	1624 s		368 s
Hpheca	3337 m	1677 s		
4	3300 m	1637 s	977 s	340 s
5	3310 m	1637 s	987 s	335 s
6	3306 m	1646 s	982 s	342 s
7	3252 m	1646 s	982 s	360 s, 315 s
Hpyra	3197 m	1701 s		
9	3295 m	1619 s	987 s	355 m, 320 m

[a] ν(C≡N) 2296 m, 2324 m. [b] In Nujol mull with cesium iodide plates. [c] ν(C≡N) 2293 m, 2321 m. [d] The spectra of the other vanadium(III) compounds, namely **8** and **10**, could not be recorded because of their decomposition even in Nujol mull.

Chart 2. Proposed Structure of Complex 7



the terminal V−Cl stretching vibration in an octahedral enviroment.[26,27] Bands at 315 (for **7**) and 320 cm^{-1} (for **9**) can be assigned to a bridging V−Cl stretching vibration.[27] Thus, the far-IR spectra seem incompatible with a monomeric skeleton; they can be explained on the basis of a dimeric chloro-bridged structure, while the complexes still have terminal V−Cl bonds (Chart 2). Compounds **8** and **10** do decompose, as it is evident from color change, even in dried Nujol and so their IR spectra were not recorded.

Electronic Spectra. Table 9 lists the spectral data for the organic ligands and their oxovanadium(IV/V) compounds. Vanadium(III) compounds were very unstable in solution and very quickly oxidized to their oxovanadium(IV)analogues; so it was not possible to obtain any spectra of the vanadium(III) species in solution.

The spectra of oxovanadium(IV) complexes **2**, **7**, and **9** in CH_3CN show only one peak in the visible region due to d−d electron transitions from the three expected. The rest of the peaks are probably obscured from the strong absorption in the UV region assigned as ligand-to-metal charge-transfer transitions observed at 350, 395 and 287 nm, respectively. From the cw EPR spectra of the compounds **7** and **9** in CH_3CN (vide supra), it is evident that these compounds exist as monomers in solution.

The visible region of complex **1** [the oxovanadium(V) complex] is dominated by an intense absorption ($\epsilon = 1800$ M^{-1} cm^{-1}) at 438 nm in CH_2Cl_2 and at 456 nm ($\epsilon = 650$ M^{-1} cm^{-1}) in CH_3NO_2. This absorption is assigned as ligand-to-metal charge transfer. Such transition has also been observed for $[VOCl_4]^-$ at 487 nm ($\epsilon = 4500$ M^{-1} cm^{-1}).[28] Another strong ligand(amide)-to-metal charge-transfer absorption is observed at 349 nm and is similar to the absorption observed for the oxovanadium(IV) complex **2**. In contrast to **1**, complexes **4**−**6** did not have any absorption in the visible region. In the UV region the spectra show a similar to **1** ligand(amide)-to-metal charge-transfer transitions at 285, 308, and 308 nm for the complexes **4**−**6**, respectively.

Table 9. UV−Visible Spectral Data for the Oxovanadium(IV/V) compounds **1**, **2**, **4**−**7**, and **9**

compound	solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
Hpycan	CH_2Cl_2	271 (12 500), 224 (11 400), 200 (3200)
Hpheca	CH_3CN	276 (8500), 221 (11 000), 196 (22 600)
Hpyra	CH_3OH	276 (4900), 235 (9200), 201 (3600)
1	CH_2Cl_2	438 (1800), 349 (9200), 274 (19 400), 219 (22 000)
	CH_3NO_2	456 (650), 367 (5300)
2	CH_3CN	642 (100), 350 (15 000), 270 (24 000), 220 (24 500), 192 (44 000)
	CH_3NO_2	383 (2600)
4	CH_3CN	285 (sh) (3400), 268 (3600), 220 (6700), 195 (18 300)
5	CH_3CN	308 (2600), 263 (2400), 220 (5600), 195 (15 300)
6	CH_3CN	308 (6000), 263 (5600), 220 (12 700), 193 (38 000)
7	CH_3CN	716 (110), 395 (1000), 294 (10 200), 197 (33 500)
	CH_3NO_2	680 (130), 353 (8000)
9	CH_3OH	287 (11 100), 233 (19 600), 202 (17 800)
	CH_3CN	716 (40), 287 (4900), 230 (91 500), 196 (19 000)

Conclusion

A series of vanadium(III) and oxovanadium(IV/V) compounds, containing the V−O_{amide} bond, was synthesized and characterized both in solid and solution state as well. These vanadium compounds are models for the interaction of vanadium with the carbonyl oxygen of the −NHCO− functionality.

The X-ray structures of the oxovanadium(IV/V) compounds **1**, **2**, and **4** showed coordination of the vanadium atom with the amide oxygen of the −NHCO− group. The shift of about 40 cm^{-1} of ν(C=O) band in these compounds as well as for all vanadium compounds induced from the coordination of the amide carbonyl oxygen with the vanadium atom and the average vanadium(IV/V)−O_{amide} bond distance of ~2.20 Å, are indicative of a reasonably strong interaction between the vanadium atom and the carbonyl oxygen of the amide group in the solid state. All known crystal structures of oxovanadium(IV/V) compounds, containing a V−O_{amide} mode of coordination, showed that the carbonyl oxygen is always coordinated to vanadium atom in a position trans to the O^{2-} ligand. There is only one exception to this general trend, where the tripodal ligand imposes the *cis*-coordination. Apparently the carbonyl amide oxygen atom has to be the weaker donor atom compared to the rest of the atoms participating in the vanadium coordination sphere, such as pyridine, amine nitrogens, chlorines and nitrogen and oxygen atoms of the ligand H_2NO^-.

Solution studies (NMR) in organic solvents revealed that the oxovanadium(V) compounds retain their solid-state structure. The ^{13}C NMR spectrum shows that the interaction of the carbonyl amide oxygen in solution is not a strong one (CIS = ~0.5 ppm). In addition, these complexes are hydrolytically unstable. Their hydrolytic stability varies significantly depending

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on the nature of the ligands co-coordinated to oxovanadium(V) center. The alkoxy ligands stabilize better the amide complexes than the chlorines. The oxovanadium(IV) compounds are also hydrolytically unstable, while vanadium(III) compounds are quite easily oxidized to give their oxovanadium(IV) analogues.

Vanadium(IV/V) is known to be essential for the function of two enzymes[2c] and also that it binds to various proteins resulting in inhibition or activation of enzymes.[29] The binding of a metal by a protein could involve the −NHCO− groups of the peptide chain backbone. The model studies of vanadium complexes (both in solution and solid state) with the amide (peptide) functionality provide evidence that the $V-O_{peptide}$ binding is a possible mode of action in proteins. The chemical properties of these complexes such as hydrolytic stability are modified from the ligands co-coordinated to vanadium atom. Apparently the stability of the $V-O_{peptide}$ bond, resulting from the interaction of vanadium with a protein, will be dependent on the coordination to vanadium of other functionalities from protein and the rigidity of the protein as well.

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Supporting Information Available: Tables listing atomic positional ($\times 10^4$) parameters of non-H atoms, positional and isotropic thermal parameters of the hydrogen atoms, anisotropic thermal parameters of the non-H atoms, bond lengths, and bond angles associated with complex **4** (4 pages). Ordering information is given on any current masthead page.

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