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Article

Monomeric Oxovanadium(IV) Compounds of the General Formula *cis*-$[\mathrm{V^{IV}({=}O)(X)(L_{NN})_2}]^{+/0}$ $\{\mathrm{X} = \mathrm{OH^-}, \mathrm{Cl^-}, \mathrm{SO_4^{2-}}$ and $\mathrm{L_{NN}} =$ 2,2′-Bipyridine (Bipy) or 4,4′-Disubstituted Bipy$\}$

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Reaction of $[\mathrm{V^{IV}OCl_2(THF)_2}]$ in aqueous solution with 2 equiv of $\mathrm{AgBF_4}$ or $\mathrm{AgSbF_6}$ and then with 2 equiv of 2,2′-bipyridine (bipy), 4,4′-di-*tert*-butyl-2,2′-bipyridine (4,4′-dtbipy), or 4,4′-di-methyl-2,2′-bipyridine (4,4′-dmbipy) affords compounds of the general formula *cis*-$[\mathrm{V^{IV}O(OH)(L_{NN})_2}]\mathrm{Y}$ $\{$where $\mathrm{L_{NN}}$ = bipy, $\mathrm{Y} = \mathrm{BF_4^-}$ (**1**), $\mathrm{L_{NN}}$ = 4,4′-dtbipy, $\mathrm{Y} = \mathrm{BF_4^-}$ (**2**$\cdot 1.2\mathrm{H_2O}$), $\mathrm{L_{NN}}$ = 4,4′-dmbipy, $\mathrm{Y} = \mathrm{BF_4^-}$ (**3**$\cdot 2\mathrm{H_2O}$), and $\mathrm{L_{NN}}$ = 4,4′-dtbipy, $\mathrm{Y} = \mathrm{SbF_6^-}$ (**4**)$\}$. Sequential addition of 1 equiv of $\mathrm{Ba(ClO_4)_2}$ and then of 2 equiv of bipy to an aqueous solution containing 1 equiv of $\mathrm{V^{IV}OSO_4{\cdot}5H_2O}$ yields *cis*-$[\mathrm{V^{IV}O(OH)(bipy)_2}]\mathrm{ClO_4}$ (**5**). The monomeric compounds **1**–**5** contain the *cis*-$[\mathrm{V^{IV}O(OH)}]^+$ structural unit. Reaction of 1 equiv of $\mathrm{V^{IV}OSO_4{\cdot}5H_2O}$ in water and of 1 equiv of $[\mathrm{V^{IV}OCl_2(THF)_2}]$ in ethanol with 2 equiv of bipy gives the compounds *cis*-$[\mathrm{V^{IV}O(OSO_3)(bipy)_2}]{\cdot}\mathrm{CH_3OH}{\cdot}1.5\mathrm{H_2O}$ (**6**$\cdot\mathrm{CH_3OH}\cdot 1.5\mathrm{H_2O}$) and *cis*-$[\mathrm{V^{IV}OCl(bipy)_2}]\mathrm{Cl}$ (**7**), respectively, while reaction of 1 equiv of $[\mathrm{V^{IV}OCl_2(THF)_2}]$ in $\mathrm{CH_2Cl_2}$ with 2 equiv of 4,4′-dtbipy gives the compound *cis*-$[\mathrm{V^{IV}OCl(4,4'\text{-}dtbipy)_2}]\mathrm{Cl}{\cdot}0.5\mathrm{CH_2Cl_2}$ (**8**$\cdot 0.5\mathrm{CH_2Cl_2}$). Compounds *cis*-$[\mathrm{V^{IV}O(BF_4)(4,4'\text{-}dtbipy)_2}]\mathrm{BF_4}$ (**9**), *cis*-$[\mathrm{V^{IV}O(BF_4)(4,4'\text{-}dmbipy)_2}]\mathrm{BF_4}$ (**10**), and *cis*-$[\mathrm{V^{IV}O(SbF_6)(4,4'\text{-}dtbipy)_2}]\mathrm{SbF_6}$ (**11**) were synthesized by sequential addition of 2 equiv of 4,4′-dtbipy or 4,4′-dmbipy and 2 equiv of $\mathrm{AgBF_4}$ or $\mathrm{AgSbF_6}$ to a dichloromethane solution containing 1 equiv of $[\mathrm{V^{IV}OCl_2(THF)_2}]$. The crystal structures of **2**$\cdot 1.2\mathrm{H_2O}$, **6**$\cdot\mathrm{CH_3OH}\cdot 1.5\mathrm{H_2O}$, and **8**$\cdot 0.5\mathrm{CH_2Cl_2}$ were demonstrated by X-ray diffraction analysis. Crystal data are as follows: Compound **2**$\cdot 1.2\mathrm{H_2O}$ crystallizes in the orthorhombic space group *Pbca* with (at 298 K) $a = 21.62(1)$ Å, $b = 13.33(1)$ Å, $c = 27.25(2)$ Å, $V = 7851(2)$ Å^3, $Z = 8$. Compound **6**$\cdot\mathrm{CH_3OH}\cdot 1.5\mathrm{H_2O}$ crystallizes in the monoclinic space group $P2_1/a$ with (at 298 K) $a = 12.581(4)$ Å, $b = 14.204(5)$ Å, $c = 14.613(6)$ Å, $\beta = 114.88(1)°$, $V = 2369(1)$, $Z = 4$. Compound **8**$\cdot 0.5\mathrm{CH_2Cl_2}$ crystallizes in the orthorhombic space group $Pca2_1$ with (at 298 K) $a = 23.072(2)$ Å, $b = 24.176(2)$ Å, $c = 13.676(1)$ Å, $V = 7628(2)$ Å^3, $Z = 8$ with two crystallographically independent molecules per asymmetric unit. In addition to the synthesis and crystallographic studies, we report the optical, infrared, magnetic, conductivity, and CW EPR properties of these oxovanadium(IV) compounds as well as theoretical studies on $[\mathrm{V^{IV}O(bipy)_2}]^{2+}$ and $[\mathrm{V^{IV}OX(bipy)_2}]^{+/0}$ species ($\mathrm{X} = \mathrm{OH^-}, \mathrm{SO_4^{2-}}, \mathrm{Cl^-}$).

Introduction

Vanadium is accumulated in high concentrations in certain sea squirts[1] and mushrooms of the genus Amanita.[2] The function of vanadium in these living systems remains as yet unclear, despite the few hypotheses, which have been put forward.[3] Moreover, two classes of vanadium dependent enzymes, namely, vanadium−nitrogenases[4] and vanadate haloperoxidases,[5] have been discovered in nature. Vanadium has the ability to produce significant physiological effects, such as the inhibition of phosphate-metabolizing enzymes,[6] the stimulation of phosphomutases[7] and -isomerases,[7] anti-

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cancer activity,[8] insulinomimetic activity,[9] etc. All these facts have initiated a lightning increase in investigations into vanadium compounds the past few years.[10]

The oxovanadium(IV) cation has been extensively used in electron paramagnetic resonance (EPR), electron spin−echo envelope modulation (ESEEM), and electron nuclear double resonance (ENDOR) studies as a spin probe[11−23] of naturally occurring vanadoproteins and in proteins where the EPR silent metal atoms (Mg^{2+}, Ca^{2+}, etc.) have been substituted by $V^{IV}O^{2+}$. During the past decades, the $[V^{IV}O(bipy)_2]^{2+}$ cation has been used as an EPR[11d] reference compound for $V^{IV}O^{2+}$ species with four nitrogen atoms in the equatorial plane, but nobody reported its isolation and characterization thus far. On the other hand, the research groups[24] who studied the $V^{IV}O^{2+}$/bipy system used $V^{IV}OSO_4 \cdot 5H_2O$, in the presence of chloride or sulfate anions,[24a,c] or $[V^{IV}O(H_2O)_5](ClO_4)_2$[24b] as vanadium sources, and the reported[24] hyperfine coupling constant, A_z, ranged from ∼161 to 163×10^{-4} cm^{-1}. Thus, we decided to try to isolate and characterize this compound. To our surprise, by using $[V^{IV}OCl_2(THF)_2]$ with 2 equiv of $AgBF_4$ as well as 2 equiv of bipy, we ended up with the very interesting monomeric species *cis*-$[V^{IV}O(OH)(bipy)_2]^+$,[25] which contains the *cis*-$[V^{IV}O(OH)]^+$ core, and not with the expected $[V^{IV}O(bipy)_2]^{2+}$ cation. At this point, it is worth noting that metal species with terminal hydroxo groups are important functional units in metalloproteins.[26] The *cis*-$[M({=}O)(OH)]^{n+}$ structural unit was identified in structurally characterized vanadium haloperoxidases,[5a,b,27] and it has also been proposed as the active species in molybdoenzymes.[28] Monomeric model compounds, having M−OH units, are difficult to isolate synthetically because OH^- tends to bridge metal centers, and this explains why few such species, structurally characterized, have been reported.[29] Herein we report the synthesis of two

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series of monomeric oxovanadium(IV) compounds containing bipy or substituted bipy (L_{NN}), of general formulas *cis*-$[V^{IV}OX(L_{NN})_2]^{+/0}$ ($X = OH^-$, SO_4^{2-}, Cl^-) and *cis*-$[V^{IV}OY(L_{NN})_2]Y$ ($Y = BF_4^-$, SbF_6^-). Electronic and molecular structures of these compounds have been studied in detail. CW EPR measurements were also carried out on these oxovanadium(IV) compounds. The geometry of the $[V^{IV}O(bipy)_2]^{2+}$ species, as well as the relative stability of the cis and trans configurational isomers of the $[V^{IV}OX(bipy)_2]^{n+}$ species, $X = OH^-$, SO_4^{2-}, and Cl^-, are discussed in the light of density functional calculations.

Experimental Section

Materials. Reagent grade chemicals were obtained from Aldrich and used without further purification. $[V^{IV}OCl_2(THF)_2]$[30] was prepared according to literature procedure. The purity of the above molecule was confirmed by elemental analysis (C, H, N, and V) and infrared spectroscopy. Reagent grade dichloromethane and acetonitrile were dried and distilled over calcium hydride, while toluene was dried and distilled over sodium wire. Methyl alcohol was dried by refluxing over magnesium methoxide. Syntheses, distillations, crystallization of the complexes, and spectroscopic characterization were performed under high-purity argon, using standard Schlenk techniques.

C, H, and N analyses were conduced by the University of Ioannina's microanalytical service. Vanadium was determined gravimetrically as vanadium pentoxide or by atomic absorption.

***cis*-[Bis(2,2′-bipyridine)hydroxo(oxo)vanadium(IV)] Tetrafluoroborate, *cis*-$[V^{IV}O(OH)(bipy)_2]BF_4$ (1).** To a stirred aqueous solution (10 mL, pH ≈ 1) of $[V^{IV}OCl_2(THF)_2]$ (0.79 g, 2.80 mmol) was added $AgBF_4$ (1.09 g, 5.60 mmol) in one portion. After the removal by filtration of the AgCl, the filtrate was treated with 2,2′-bipyridine (0.87 g, 5.60 mmol). Upon addition of 2,2′-bipyridine, the blue color of the solution changed to red-brown, and a yellow-brown precipitate was formed; the pH of the solution changed to ≈4. The mixture was stirred for 1 h, and the yellow-brown solid was filtered off, washed with 2-propanol (2 × 5 mL), and dried under vacuum to yield 1.16 g (86%) of the product. Crystals of **1** suitable for X-ray structure analysis were obtained by slow evaporation of a concentrated solution of **1** in acetonitrile/methanol (1:1 v/v). Anal. Calcd for $C_{20}H_{17}BF_4N_4O_2V$ (483.13): C, 49.72; H, 3.55; N, 11.60; V, 10.54. Found: C, 49.63; H, 3.54; N, 11.42; V, 10.62. $\mu_{eff} = 1.75\ \mu_B$ at 298 K.

***cis*-[Bis(4,4′-di-*tert*-butyl-2,2′-bipyridine)hydroxo(oxo)vanadium(IV)] Tetrafluoroborate, *cis*-$[V^{IV}O(OH)(4,4'\text{-dtbipy})_2]BF_4\cdot 1.2H_2O$ ($2\cdot 1.2H_2O$).** Compound $\mathbf{2}\cdot 1.2H_2O$ was prepared in a fashion similar to that used for **1** except that 4,4′-di-*tert*-butyl-2,2′-bipyridine was used instead of 2,2′-bipyridine. The product, a yellow solid, was obtained in 85% yield. Crystals of $\mathbf{2}\cdot 1.2H_2O$ suitable for X-ray structure analysis were obtained by slow evaporation of a concentrated solution of $\mathbf{2}\cdot 1.2H_2O$ in dichloromethane/toluene (1:1 v/v). Anal. Calcd for $C_{36}H_{51.4}BF_4N_4O_{3.2}V$ (729.17): C, 59.29; H, 7.10; N, 7.68; V, 6.98. Found: C, 59.00; H, 6.55; N, 7.67; V, 6.89. $\mu_{eff} = 1.72\ \mu_B$ at 298 K.

***cis*-[Bis(4,4′-di-methyl-2,2′-bipyridine)hydroxo(oxo)vanadium(IV)] Tetrafluoroborate, *cis*-$[V^{IV}O(OH)(4,4'\text{-dmbipy})_2]BF_4\cdot 2H_2O$ ($3\cdot 2H_2O$).** Compound $\mathbf{3}\cdot 2H_2O$ was prepared in a fashion similar to that used for **1** except that 4,4′-dimethyl-2,2′-bipyridine was used instead of 2,2′-bipyridine. The product, a yellow-brown solid, was obtained in 76% yield. Anal. Calcd for $C_{24}H_{27}BF_4N_4O_4V$ (575.26): C, 50.11; H, 5.08; N, 9.74; V, 8.85. Found: C, 49.60; H, 4.69; N, 9.45; V, 8.55. $\mu_{eff} = 1.70\ \mu_B$ at 298 K.

***cis*-$[V^{IV}O(OH)(4,4'\text{-dtbipy})_2]SbF_6$ (4).** Compound **4** was prepared in a fashion similar to that used for **1** except that (i) $AgSbF_6$ was used instead of $AgBF_4$, and (ii) 4,4′-di-*tert*-butyl-2,2′-bipyridine was used instead of 2,2′-bipyridine. The product, a yellow solid, was obtained in 78% yield. Anal. Calcd for $C_{36}H_{49}F_6N_4O_2SbV$ (856.49): C, 50.48; H, 5.77; N, 6.54; V, 5.94. Found: C, 51.05; H, 5.60; N, 6.24; V, 6.12. $\mu_{eff} = 1.67\ \mu_B$ at 298 K.

***cis*-$[V^{IV}O(OH)(bipy)_2](ClO_4)$ (5).** To a stirred aqueous solution (10 mL, pH ≈ 1.5) of $V^{IV}OSO_4\cdot 5H_2O$ (0.25 g, 1.00 mmol) was added in one portion solid $Ba(ClO_4)_2$ (0.34 g, 1.00 mmol). After the mixture was stirred for 1 h, the white solid $BaSO_4$ was separated by filtration, and 2,2′-bipyridine (0.31 g, 2.00 mmol) was added to the blue filtrate. Upon addition of 2,2′-bipyridine the color of the solution changed to brown, a brown solid was formed, and the pH of the solution changed to ≈4. The reaction mixture was stirred for 1 h at room temperature before being filtered, and the precipitate was washed with methanol (2 × 5 mL) and diethyl ether (2 × 5 mL), and dried under vacuum to yield 0.39 g (78%) of the product. Anal. Calcd for $C_{20}H_{17}ClN_4O_6V$ (495.77): C, 48.45; H, 3.46; N, 11.30; V, 10.27. Found: C, 48.15; H, 3.52; N, 11.13; V, 10.20. $\mu_{eff} = 1.74\ \mu_B$ at 298 K.

***cis*-$[V^{IV}O(SO_4)(bipy)_2]\cdot CH_3OH\cdot 1.5H_2O$ ($6\cdot CH_3OH\cdot 1.5H_2O$).** To a stirred aqueous solution (5 mL, pH ≈ 1.5) of $V^{IV}OSO_4\cdot 5H_2O$ (1.52 g, 6.00 mmol) was added in one portion 2,2′-bipyridine (1.87 g, 12.00 mmol). Upon addition of the 2,2′-bipyridine, the blue solution became green. Then, over 1 h of magnetic stirring methanol (20 mL) was added to it, and the mixture was left at 4 °C for 3 days to obtain 1.80 g (56%) of crystalline product. The crystalline product was suitable for X-ray structure analysis. Anal. Calcd for $C_{21}H_{23}N_4O_{7.5}SV$ (534.44): C, 47.19; H, 4.34; N, 10.48; V, 9.53. Found: C, 47.04; H, 4.25; N, 10.47; V, 9.80. $\mu_{eff} = 1.70\ \mu_B$ at 298 K.

***cis*-$[V^{IV}OCl(bipy)_2]Cl$ (7).** 2,2′-Bipyridine (0.312 g, 2.00 mmol) was added in one portion to a stirred solution of $[V^{IV}OCl_2(THF)_2]$ (0.282 g, 1.00 mmol) in ethanol (5 mL). Upon addition of the 2,2′-bipyridine, the blue color of the solution became green. Then, after over 1 h of magnetic stirring, a light green precipitate was formed, which was filtered off, washed with cold ethanol (2 × 5 mL) and diethyl ether (2 × 5 mL), and dried in vacuo to afford 0.36 g (80%) of **7**. Anal. Calcd for $C_{20}H_{16}Cl_2N_4OV$ (450.22): C, 53.36; H, 3.58; N, 12.44; V, 11.32. Found: C, 53.47; H, 3.80; N, 11.98; V, 11.58. $\mu_{eff} = 1.66\ \mu_B$ at 298 K.

***cis*-$[V^{IV}OCl(4,4'\text{-dtbipy})_2]Cl\cdot 0.5CH_2Cl_2$ ($8\cdot 0.5CH_2Cl_2$).** Solid 4,4′-di-*tert*-butyl-2,2′-bipyridine (0.54 g, 2.00 mmol) was added in one portion to a stirred suspension of $[V^{IV}OCl_2(THF)_2]$ (0.282 g, 1.00 mmol) in dichloromethane (10 mL). Upon addition of 4,4′-di-*tert*-butyl-2,2′-bipyridine, the solution cleared, and its light blue color changed to green. After being stirred for 1 h, the reaction mixture was evaporated to dryness, and the green solid was triturated with diethyl ether (2 × 5 mL) and dried under vacuum to get 0.69 g (97%) of $\mathbf{8}\cdot 0.5CH_2Cl_2$. Crystals of $\mathbf{8}\cdot 0.5CH_2Cl_2$ suitable for X-ray structure analysis were obtained by slow evaporation of a concentrated solution of $\mathbf{8}\cdot 0.5CH_2Cl_2$ in dichloromethane/toluene (3:1 v/v). Anal. Calcd for $C_{36.5}H_{49}Cl_3N_4OV$ (717.12): C, 61.13; H, 6.87; N, 7.81; V, 7.10. Found: C, 62.20; H, 7.25; N, 7.87; V, 7.22. $\mu_{eff} = 1.73\ \mu_B$ at 298 K.

***cis*-$[V^{IV}O(BF_4)(4,4'\text{-dtbipy})_2]BF_4$ (9).** 4,4′-Di-*tert*-butyl-2,2′-bipyridine (0.54 g, 2.00 mmol) in one portion and solid $AgBF_4$ (0.312 g, 2.00 mmol) were successively added to a stirred suspension of $[V^{IV}OCl_2(THF)_2]$ (0.282 g, 1.00 mmol) in dichloromethane (10 mL). The mixture was stirred, in the absence of

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light at room temperature, under argon for 24 h. The resulting mixture was filtered off, to separate the white solid (AgCl), and the filtrate was evaporated to dryness. The green solid was triturated with diethyl ether (2 × 5 mL) and dried in vacuo to get 0.75 g (97%) of **9**. Anal. Calcd for $C_{36}H_{48}B_2F_8N_4OV$ (777.35): C, 55.62; H, 6.22; N, 7.21; V, 6.55. Found: C, 54.25; H, 6.63; N, 6.90; V, 6,60. $\mu_{eff} = 1.68\ \mu_B$ at 298 K.

***cis*-[V^{IV}O(BF$_4$)(4,4′-dmbipy)$_2$]BF$_4$ (10).** Compound **10** was prepared in a fashion similar to that used for complex **9** except that 4,4′-dimethyl-2,2′-bipyridine was used instead of 4,4′-di-*tert*-butyl-2,2′-bipyridine. The product was obtained in 95% yield. Anal. Calcd for $C_{24}H_{24}B_2F_8N_4OV$ (609.03): C, 47.33; H, 3.97; N, 9.20; V, 8.36. Found: C, 46.46; H, 4.41; N, 8.82; V, 8.45. $\mu_{eff} = 1.73\ \mu_B$ at 298 K.

***cis*-[V^{IV}O(SbF$_6$)(4,4′-dtbipy)$_2$]SbF$_6$ (11).** Compound **11** was prepared in a fashion similar to that used for complex **9** except that $AgSbF_6$ was used instead of $AgBF_4$. The product, a green solid, was obtained in 96% yield. Anal. Calcd for $C_{36}H_{48}F_{12}N_4OSb_2V$ (1075.22): C, 40.21; H, 4.50; N, 5.21; V, 4.74. Found: C, 41.03; H, 5.20; N, 4.77; V, 4.98. $\mu_{eff} = 1.70\ \mu_B$ at 298 K.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR in KBr pellets or Nujol with KBr windows, while far-IR spectra were recorded in polyethylene pellets. Electronic absorption spectra were measured as solution in septum-sealed quartz cuvettes on a Jasco V-530 UV−vis spectrophotometer. 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. Solution conductivity data were collected in dichloromethane, acetonitrile, methyl alcohol, and water using a Tacussel electronic CD 6NG conductivity bridge. A temperature of 25 °C was maintained by constant-temperature bath. The cell constant was determined to be $\kappa = 1.1025\ \text{cm}^{-1}$ by using a 0.02 M aqueous solution of potassium chloride to calibrate the conductivity cell. The molar concentration of the $V^{IV}O^{2+}$ compounds was 1×10^{-3} M.

EPR Studies. Continuous-wave EPR spectra were recorded at a liquid helium temperatures (20 K) or at 110 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 Brucker 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 WIN-EPR, for an $S = {}^1/_2$ electron spin coupled to the $I = {}^7/_2$ nuclear spin from the ^{51}V nucleus.

Computational Details. The electronic structure and geometries of the actual and the model complexes studied were computed within the density functional theory using gradient corrected functionals, at the Becke3LYP computational level.[31,32] The effective core potential (ECP) approximation of Hay and Wadt was used.[33] For V atom, the electrons described by the ECP were those of 1s, 2s, and 2p shells. The basis set used was of valence double-ζ quality.[34] Full geometry optimizations were carried out without symmetry constraints. In the model complexes, the bipyridine ligand was replaced by the model ligand [HN═CH−CH═NH], L, which has the same donor atoms and resembles well with the conjugated system of bipyridine. All the calculations were performed using the Gaussian-98 package.[35]

Table 1. Summary of Crystal, Intensity Collection, and Refinement Data for **2**·1.2H$_2$O, **6**·CH$_3$OH·1.5H$_2$O, and **8**·0.5CH$_2$Cl$_2$

	2·1.2H$_2$O	**6**·CH$_3$OH·1.5H$_2$O	**8**·0.5CH$_2$Cl$_2$
empirical formula	$C_{36}H_{51.4}BF_4$-$N_4O_{3.2}V$	$C_{21}H_{23}N_4O_{7.5}SV$	$C_{36.5}H_{49}Cl_3$-N_4OV
fw	729.16	534.43	717.12
T, K	298	298	298
radiation; λ, Å	Mo Kα; 0.71073	Mo Kα; 0.71073	Cu Kα; 1.54180
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*Pbca*	$P2_1/a$	$Pca2_1$
a (Å)	21.62(1)	12.581(4)	23.072(2)
b (Å)	13.33(1)	14.204(5)	24.176(2)
c (Å)	27.25(2)	14.613(6)	13.676(1)
β (deg)		114.88(1)	
V (Å^3)	7851(2)	2369(1)	7628(2)
Z	8	4	8
d_{calcd}/d_{measd} (g cm^{-3})	1.234/1.22	1.499/1.48	1.249/1.23
abs coeff μ (mm^{-1})	0.310	0.559	4.355
octants collected	*h*, ±k, ±l	±h, k, l	*h*, *k*, ±l
GOF on F^2	1.148	1.081	1.035
R indices	R1^a = 0.1121 wR2^{b,c} = 0.2907	R1^a = 0.0555 wR2^{b,d} = 0.1573	R1^a = 0.1247 wR2^{b,e} = 0.3188

[a] $R1 = \{\{\Sigma||F_o| - |F_c||\}\}/\{\Sigma(|F_o|)\}$. [b] $wR2 = \sqrt{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]}$. [c] For 4038 reflections with $I > 2\sigma(I)$. [d] For 3454 reflections with $I > 2\sigma(I)$. [e] For 4763 reflections with $I > 2\sigma(I)$.

X-ray Crystallography: Crystal Structure Determination. A red crystal of **2**·1.2H$_2$O (0.15 × 0.25 × 0.50 mm^3), a red crystal of **6**·CH$_3$OH·1.5 H$_2$O (0.15 × 0.15 × 0.50 mm^3), and a green crystal of **8**·0.5CH$_2$Cl$_2$ (0.12 × 0.30 × 0.45 mm^3) were mounted in capillaries with drops of mother liquor to prevent solvent loss and destruction of the crystals. Diffraction measurements for **2**·1.2H$_2$O and **6**·CH$_3$OH·1.5H$_2$O were made on a Crystal Logic Dual Goniometer diffractometer, using graphite monochromated Mo Kα radiation, while **8**·0.5CH$_2$Cl$_2$ was mounted on a $P2_1$ Nicolet diffractometer upgraded by Crystal Logic, using graphite monochromated Cu Kα radiation. The crystals of compounds **2**·1.2H$_2$O and **8**·0.5CH$_2$Cl$_2$ showed poor diffraction, and repeated efforts to improve them proved unsuccessful. Thus, we proceeded with data collection in order to determine the coordination geometry around vanadium and to establish the cis orientation of the hydroxo/chloro ligands in **2**·1.2H$_2$O/**8**·0.5CH$_2$Cl$_2$**,** respectively, with respect to the oxo group. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11° < 2\theta < 23°$ (for **2**·1.2H$_2$O and **6**·CH$_3$OH·1.5H$_2$O) and $22° < 2\theta < 54°$ (for **8**·0.5CH$_2$Cl$_2$). Crystallographic details are given in Table 1. Intensity data were measured by using $\theta - 2\theta$ scans. Three standard reflections were monitored every 97 reflections, over the course of data collection. They showed less than 3% variation and no decay. Lorentz polarization (for all) and ψ-scan

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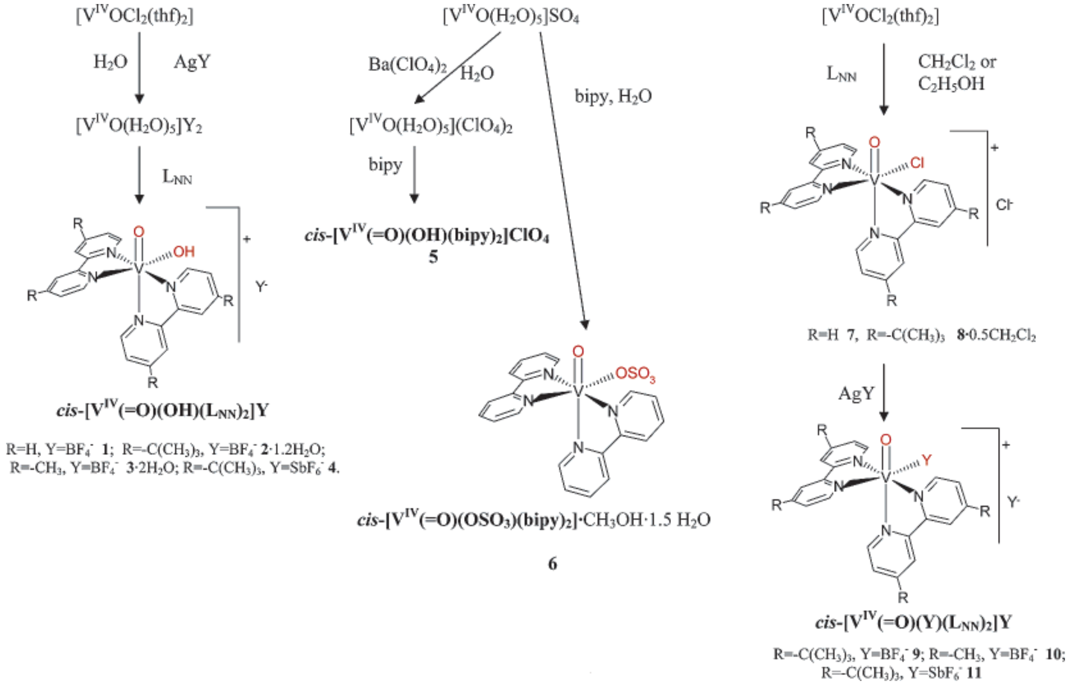
Scheme 1. Synthesis of Compounds **1**−**11** and Molecular Drawings of Them



absorption (for **2**·1.2H_2O only) corrections were applied by using Crystal Logic software. Further experimental crystallographic details for **2**·1.2H_2O: $2\theta_{max} = 46°$, scan speed 1.2°/min; scan range 2.2 + $\alpha_1\alpha_2$ separation; reflections collected/unique/used, 8987/5426-(R_{int} = 0.0503)/5424; 462 parameters refined; $(\Delta/\sigma)_{max} = 0.004$; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 0.826/-0.338 e/Å^3; R/R_w (for all data), 0.1408/0.3169. Further experimental crystallographic details for **6**·CH_3OH·1.5H_2O: $2\theta_{max} = 50°$, scan speed 3.2°/min; scan range 2.2 + $\alpha_1\alpha_2$ separation; reflections collected/unique/used, 4349/4178(R_{int} = 0.0236)/4178; 380 parameters refined; $(\Delta/\sigma)_{max} = 0.013$; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 0.733/-0.598 e/Å^3; R/R_w (for all data), 0.0658/0.1713. Further experimental crystallographic details for **8**·0.5CH_2Cl_2: $2\theta_{max}$ = 93°, scan speed 1.5°/min; scan range 2.4 + $\alpha_1\alpha_2$ separation; reflections collected/unique/used, 6578/6574 (R_{int} = 0.0818)/6572; 777 parameters refined; $(\Delta/\sigma)_{max} = 0.122$; $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ = 0.717/−0.637 e/Å^3; R/R_w (for all data), 0.1572/0.3756.

The structure of all three complexes was solved by direct methods using SHELXS-86.[36] Refinement was achieved by full-matrix least-squares techniques on F^2 with SHELXL-93.[37] All non-H atoms in the structure of **2**·1.2H_2O were refined anisotropically (except the water solvent molecules which were refined isotropically with occupation factors fixed at 0.70 and 0.50, respectively); all H-atoms were introduced at calculated positions as riding on bonded atoms (except those of the methyl carbon atoms C(16), C(17), and C(18) which were not included in the refinement). The fluorine atoms of the BF_4^- counterion were found disordered and were refined anisotropically in two orientations with occupation factors summing to one (0.55 and 0.45, respectively). All non-H atoms in the structure of **6**·CH_3OH·1.5H_2O were refined anisotropically; all H-atoms were located by difference maps and were refined isotropically (except those of the solvent molecules which were not included in the refinement). Compound **8**·0.5CH_2Cl_2 crystallizes in the noncentrosymmetric orthorhombic space group $Pca2_1$ [a = 23.072(2) Å, b = 24.176(2) Å, c = 13.676(1) Å, V = 7628(2) Å^3, Z = 8] with two crystallographically independent molecules per asymmetric unit. The tertbutyl groups and the dichloromethane solvent molecules were refined isotropically; all the rest of the non-H atoms were refined anisotropically. No hydrogen atoms in the structure of **8**·0.5CH_2Cl_2 were included in the refinement.

Results and Discussion

Syntheses. The synthesis of the oxovanadium(IV) compounds **1**−**11** with bipy and 4,4′-disubstituted bipy is summarized in Scheme 1. Compounds **1**−**4** were prepared by treating an aqueous solution of [$V^{IV}OCl_2(THF)_2$] with 2 equiv of a silver salt, AgY (Y = BF_4^-, SbF_6^-), filtration of the solution to remove the precipitate (AgCl), and addition of 2 equiv of bipy, 4,4′-dtbipy, or 4,4′-dmbipy [eqs 1 and 2]. The chlorines were removed from the solution, since the anionic ligands do prefer an equatorial ligation, thus hoping to force the two chelate bipy ligands in the equatorial plane.

$$[V^{IV}OCl_2(THF)_2] + 2AgY \xrightarrow{H_2O} [V^{IV}O(H_2O)_5]Y_2 + 2AgCl\downarrow + 2THF \quad (1)$$

$$[V^{IV}(H_2O)_5]Y_2 + 2L_{NN} \xrightarrow{H_2O} cis\text{-}[V^{IV}O(OH)(L_{NN})_2]Y + HY + 4H_2O \quad (2)$$

Compound **5** was prepared by the same protocol used for the preparation of compounds **1**−**4** except that $V^{IV}OSO_4$·5H_2O and $Ba(ClO_4)_2$ were used instead of [$V^{IV}OCl_2(THF)_2$] and AgY, respectively, to prepare the perchlorate salt [$V^{IV}O(H_2O)_5](ClO_4)_2$ in solution. Compounds **6**·CH_3OH·1.5H_2O and **7**[24b] were synthesized by reacting $V^{IV}OSO_4$·5H_2O and [$V^{IV}OCl_2(THF)_2$] with 2 equiv of bipy in water and ethyl alcohol, respectively. Compound **8**·0.5CH_2Cl_2 was prepared by treating [$V^{IV}OCl_2(THF)_2$] with 2 equiv of 4,4′-dtbipy in CH_2Cl_2, while **9**−**11** were isolated by reaction of [V^{IV}-

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$OCl_2(THF)_2]$ in CH_2Cl_2 with 2 equiv of a 4,4′-disubstituted bipy and 2 equiv of a silver salt [eq 3], filtration to remove AgCl, evaporation to dryness of the filtrate, and trituration with diethyl ether of the solid.

$$[V^{IV}OCl_2(THF)_2] + 2\,L_{NN} + AgY \rightarrow cis\text{-}[V^{IV}OY(L_{NN})_2]Y + AgCl\downarrow + 2THF \quad (3)$$

Compounds **6**$\cdot CH_3OH\cdot 1.5H_2O$ and **7**, i.e., the compounds *cis*-$[V^{IV}O(OSO_3)(bipy)_2]\cdot CH_3OH\cdot 1.5H_2O$ and *cis*-$[V^{IV}OCl(bipy)_2]Cl$, were synthesized to compare their EPR spectra with those of **1**. Compound **8**$\cdot 0.5CH_2Cl_2$ resulted from the reaction of $[V^{IV}OCl_2(THF)_2]$ with 4,4′-dtbipy in CH_2Cl_2, hoping to isolate the *trans*-$[V^{IV}OCl(4,4'\text{-dtbipy})_2]^+$ species (see theoretical calculations) in this nonpolar solvent. Compounds **9**−**11** were isolated in an effort to prepare $[V^{IV}O(L_{NN})_2]^{2+}$ species in a noncoordinating solvent (CH_2Cl_2) without the presence of any nucleophilic species (the chlorines were removed by Ag^+). The 4,4′-disubstituted bipy (s-bipy) was used instead of bipy to make the oxovanadium(IV)-s-bipy species soluble in CH_2Cl_2 and, thus, to allow us to separate the vanadium compounds from AgCl [eq 3]. Our efforts to get crystals of **9**−**11** were unsuccessful thus far. Compounds **1**−**11** are stable in air in the solid state, and compounds **1**−**5** are also stable in solution (H_2O, CH_3OH, CH_3CN, etc.). Compounds **6**$\cdot CH_3OH\cdot 1.5H_2O$−**8**$\cdot 0.5CH_2Cl_2$ are stable in CH_2Cl_2 though **6**$\cdot CH_3OH\cdot 1.5H_2O$ and **7** are only slightly soluble in this solvent. Compounds **9**, **10,** and **11** are stable in dry CH_2Cl_2 under inert atmosphere, while in H_2O they decompose instantaneously to their hydroxo analogues **2**$\cdot 1.2H_2O$, **3**$\cdot 2H_2O$, and **4**, respectively [eq 4]. This is evident from the UV−vis spectra of **9**, **10**, and **11** in water which are identical with those of **2**$\cdot 1.2H_2O$, **3**$\cdot 2H_2O$, and **4** in water (see Table 2), respectively.

$$cis\text{-}[V^{IV}OY(L_{NN})_2]Y + H_2O \rightarrow cis\text{-}[V^{IV}O(OH)(L_{NN})_2]Y + HY \quad (4)$$

Electronic Spectra. Table 2 lists the spectral data for the oxovanadium(IV) compounds **1**−**11**. On the assumption of pseudo-C_{4v} symmetry for these compounds, the predicted transitions[38] are $b_2 \rightarrow e$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$), $b_2 \rightarrow b_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$), and $b_2 \rightarrow a_1$ ($d_{xy} \rightarrow d_{z^2}$). The compounds of the general formula, *cis*-$[V^{IV}O(OH)(L_{NN})_2]Y$, i.e., **1**−**5**, gave two bands at ∼750 and at ∼525 nm in H_2O and various organic solvents as well, which were assigned to $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions, respectively. Compounds **9**, **10**, and **11** of the general formula *cis*-$[V^{IV}OY(s\text{-bipy})_2]Y$ also gave two bands at ∼710 and ∼530 nm in CH_2Cl_2 (these compounds are also octahedral, see conductivity and EPR sections) which were assigned to $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions, while in H_2O their spectra were identical to their hydroxy-analogues **2**$\cdot 1.2H_2O$, **3**$\cdot 2H_2O$, and **4**, respectively. Compounds **6**$\cdot CH_3OH\cdot 1.5H_2O$−**8**$\cdot 0.5CH_2Cl_2$ in water also gave two bands at ∼730 nm and ∼530 nm, but on the basis of conductivity measurements, these compounds do decompose in this solvent. Compound **8**$\cdot 0.5CH_2Cl_2$ in CH_2Cl_2 gave two bands at 710 and 574 nm which were also assigned to $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions, respectively.

Table 2. UV−Vis Spectral Data for the Oxovanadium(IV) Compounds **1**−**11**[a]

compd	solvent	λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)
1	H_2O	752 (31), 529 (35), 300 (21 560), 270 (22 040), 229 (29 790), 205 (28 530)
	CH_3CN	744 (23), 518 (sh) (35), 304 (21 550), 245 (14 840), 205 (43 240)
2$\cdot 1.2H_2O$	H_2O	749 (56), 524 (66), 302 (29 260), 250 (sh) (19 080), 234 (40 000)
	CH_3CN	751 (20), 521 (sh) (37), 310 (sh) (23 070), 301 (27 500), 261 (9824), 253 (8551)
	CH_2Cl_2	740 (25), 525 (32), 312 (sh) (25 960), 303 (33 220), 250 (16 780), 236 (23 940)
3$\cdot 2H_2O$	H_2O	741 (53), 531 (65), 304 (28 280), 248 (sh) (19 500)
	CH_3CN	740 (23), 526 (32), 317 (sh) (24 260), 302 (27 140), 261 (9743), 254 (8412)
	CH_2Cl_2	741 (27), 526 (36), 310 (sh) (27 670), 301 (32 270), 252 (18 010), 233 (24 730)
4	H_2O	742 (53), 531 (62), 303 (28 350), 249 (sh) (19 420)
	CH_3CN	750 (18), 525 (33), 310 (sh) (25 030), 302 (29 620), 253 (10 430)
	CH_2Cl_2	742 (28), 526 (41), 311 (sh) (35 990), 303 (42 200), 252 (28 690), 233 (42 670)
5	H_2O	756 (27), 522 (sh) (35), 304 (15 640), 238 (12 360), 213 (14 290)
6$\cdot CH_3OH\cdot 1.5H_2O$	H_2O	729 (32), 531 (20), 303 (11 830), 290 (sh) (10 690), 237 (10 950)
7	H_2O	729 (43), 526 (23), 305 (18 950), 287 (sh) (14 400), 230 (15 520)
	CH_3CN	709 (37), 577 (sh) (15), 317 (sh) (15 170), 305 (21 380), 262 (6880)
	CH_3OH	714 (32), 583 (sh) (16), 305 (11 670), 294 (sh) (10 800), 243 (9190)
8$\cdot 0.5CH_2Cl_2$	CH_2Cl_2	710 (41), 574 (24), 317 (sh) (29 580), 305 (31 160), 237 (22 030)
	H_2O	740 (19), 537 (37), 312 (sh) (22 680), 305 (24 790), 236 (22 910), 210 (34 560)
9	CH_2Cl_2	708 (43), 526 (38), 304 (26 230), 248 (sh) (14 800), 233 (26 350)
	H_2O	746 (59), 526 (64), 302 (31 320), 252 (sh) (21 430), 234 (41 750)
10	CH_2Cl_2	715 (40), 541 (34), 305 (25 130), 252 (sh) (16 850), 232 (26 760)
	H_2O	740 (52), 530 (63), 302 (29 370), 247 (sh) (19 330)
11	CH_2Cl_2	712 (40), 535 (20), 307 (18 920), 250 (sh) (15 740), 234 (25 900)
	H_2O	742 (58), 531 (60), 303 (28 370), 248 (sh), (19 670)

[a] The concentration of all the oxovanadium(IV) compounds was approximately 0.02 M for the visible region of spectrum.

Infrared Spectroscopy. Assignments of some diagnostic bands are given in Table 3. The ν(O−H) bands are present in the spectra of compounds **1**−**6**$\cdot CH_3OH\cdot 1.5H_2O$ in the region ≈3400−3600 cm^{-1}. The very strong bands in the range 1620−1585 cm^{-1} correspond to C═C and C═N stretching vibrations. All the oxovanadium(IV) compounds show a strong ν(V═O) band in the range 961−985 cm^{-1}. The ν(V−Cl) stretch for **7** and **8**$\cdot 0.5CH_2Cl_2$ appears as a strong band at 361 cm^{-1} in the far-IR, while the monodentate O-ligation of SO_4^{2-} in **6**$\cdot CH_3OH\cdot 1.5H_2O$ gives characteristic bands[39] at 1147, 1030, 645, and 601 cm^{-1}. The vibrations

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(38) Ballhausen, C. J.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 111.

(39) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986, p 248.

Table 3. Characteristic Infrared Bands (cm^{-1}) of the Oxovanadium(IV) Compounds **1**−**11**

compd	ν(O−H)	ν(C=C, C=N)	ν(V=O)
1	3582w[a]	1602vs	970vs, 961vs
2·1.2H_2O	3600w,[a] 3435m	1616vs	969vs
3·2H_2O	3606w,[a] 3552w, 3492w	1619vs	969s
4	3632w	1615vs	976vs
5	3505m	1601s	962s
6·CH_3OH·1.5H_2O	3431m	1601vs	981s
7		1607m, 1600s	961vs
8·0.5CH_2Cl_2		1615vs, 1585m	971vs
9		1618s	979s
10		1618s, 1593vs	970s
11		1617s	985s

[a] These bands appear when the spectra are recorded in Nujol.

Table 4. Conductivity Values (Λ_M in Ω^{-1} cm^{-1} mol^{-1}) for a Few Characteristic Oxovanadium(IV) Compounds of the Present Study

compd	solvent	Λ_M[a]
1	CH_3CN	166
	H_2O	141
5	CH_3CN	155
	H_2O	134
6·CH_3OH·1.5H_2O	MeOH	18
	H_2O	143
7	MeOH	105
	CH_3CN	166
	H_2O	202
9	CH_2Cl_2	27
10	CH_2Cl_2	24
11	CH_2Cl_2	29

[a] Error in Λ_M values ±1.0.

of the counterions BF_4^-, SbF_6^-, and ClO_4^- were detected in a variety of regions with the most characteristic bands at ~1060, ~670, and 1100 cm^{-1}, respectively.

Conductivity. Table 4 lists the molar conductivities for a few characteristic oxovanadium(IV) compounds of the present study. A solution of **9**−**11** in dichloromethane (1×10^{-3} M) registered a molar conductivity of 27 compared to 28 Ω^{-1} cm^{-1} mol^{-1} for $[(n\text{-Bu})_4N]BF_4$ at the same concentration at 25 °C. Thus, compounds **9**−**11** in CH_2Cl_2 are 1:1 electrolytes, and this means that one counterion (BF_4^-, or SbF_6^-) is presumably ligated to vanadium through one fluorine atom. The ligation of a fluorine atom to vanadium in **9**−**11** is supported by EPR data as well (see EPR discussion). Compounds **1** and **5** are 1:1 electrolytes in both CH_3CN and H_2O (Table 4). The molar conductivity of **6**·CH_3OH·1.5H_2O in H_2O is indicative of the full dissociation of the sulfate ligand from the vanadium atom, while its molar conductivity in CH_3OH, which is a less polar solvent than H_2O, is indicative of a partial dissociation of the sulfate anion. Compound **7** behaves as 1:1 electrolyte in CH_3OH and CH_3CN, while in H_2O it behaves as 1:2 electrolyte (Table 4).

X-ray Crystal Structures. The molecular structures of compounds **1**,[25] **2**·1.2H_2O, **6**·CH_3OH·1.5H_2O, and **8**·0.5CH_2Cl_2 are shown as ORTEP diagrams in Figures 1−4, respectively. Selected bond distances and angles for **2**·1.2H_2O and **6**·CH_3OH·1.5H_2O are listed in Table 5. In all four compounds, the coordination geometry about the vanadium atom is best described as distorted octahedral comprised of the doubly bonded oxygen atom, four nitrogen atoms from the neutral chelate ligands, and a monodentate ligand fulfilling the octahedral requirements of the metal. The monodentate ligand in compound **6**·CH_3OH·1.5H_2O is the SO_4^{2-} ion, so the complex is neutral. In the cases of compounds **2**·1.2H_2O and **8**·0.5CH_2Cl_2, the monodentate ligand is the hydroxo and chloro ions, respectively, so the complexes are cationic and neutralized by BF_4^- and Cl^- ions, respectively. The most important feature in the structure of compounds **2**·1.2H_2O, **6**·CH_3OH·1.5H_2O, and **8**·0.5CH_2Cl_2 is the cis orientation of the oxo group with respect to the monodentate ligands OH^-, SO_4^{2-}, and Cl^-, respectively. The

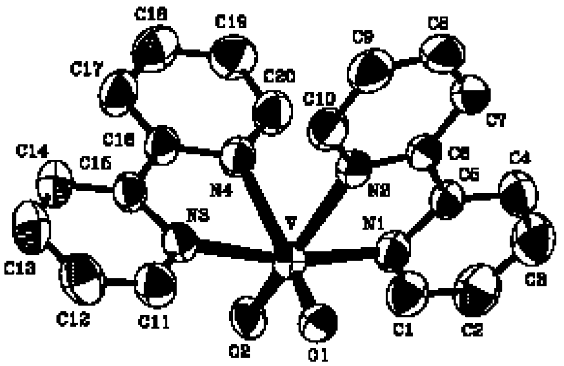


Figure 1. ORTEP drawing of the molecular structure of **1** showing the atom labeling scheme. Atoms are represented by their 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity (from ref 25).

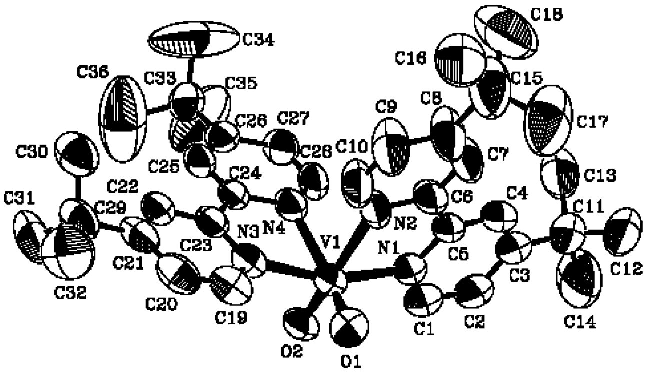


Figure 2. ORTEP diagram of **2**·1.2H_2O with 50% thermal probability ellipsoids showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity.

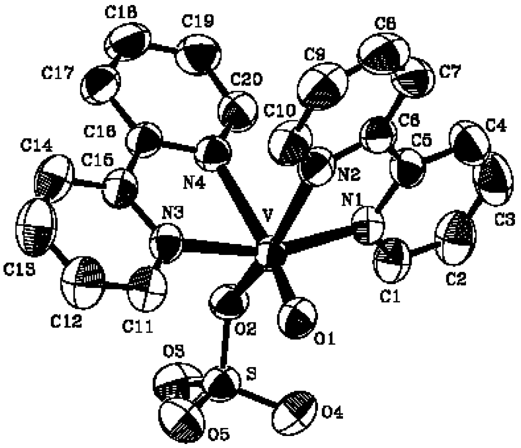


Figure 3. Molecular structure and atom numbering scheme of **6**·CH_3OH·1.5H_2O with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

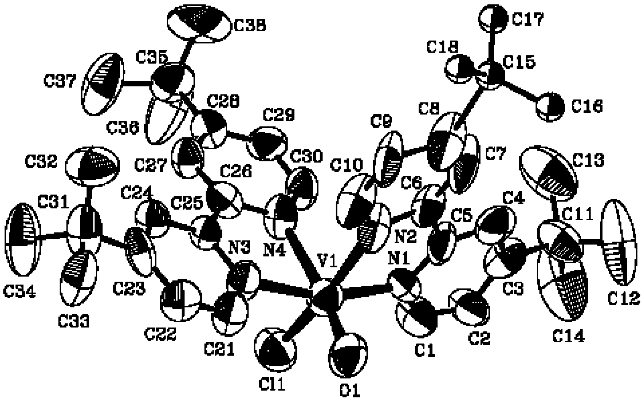


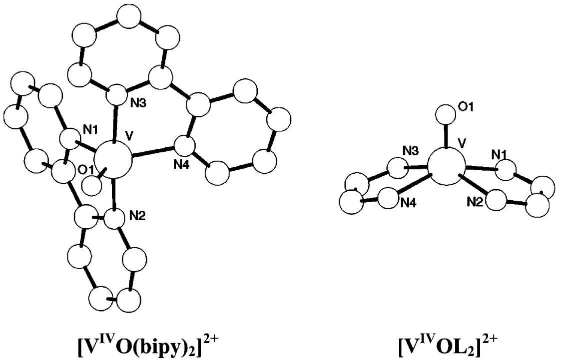
Figure 4. Molecular structure and atom numbering scheme of $\mathbf{8}\cdot 0.5CH_2Cl_2$ with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 5. Selected Interatomic Bond Distances (Å) and Angles (deg) for the Compounds $\mathbf{2}\cdot 1.2H_2O$ and $\mathbf{6}\cdot CH_3OH\cdot 1.5H_2O$

	$\mathbf{2}\cdot 1.2H_2O$	$\mathbf{6}\cdot CH_3OH\cdot 1.5H_2O$		$\mathbf{2}\cdot 1.2H_2O$	$\mathbf{6}\cdot CH_3OH\cdot 1.5H_2O$
V−O(1)	1.659(6)	1.584(2)	V−N(2)	2.179(6)	2.142(3)
V−O(2)	1.785(5)	1.957(2)	V−N(3)	2.116(6)	2.117(3)
V−N(1)	2.107(6)	2.100(3)	V−N(4)	2.261(6)	2.296(3)
O(1)−V−O(2)	104.1(3)	105.0(1)	N(1)−V−N(2)	75.0(2)	76.41(1)
O(1)−V−N(1)	101.2(3)	101.9(1)	N(3)−V−N(2)	92.9(2)	92.2(1)
O(2)−V−N(1)	91.7(2)	92.4(1)	O(1)−V−N(4)	165.9(3)	166.5(1)
O(1)−V−N(3)	93.2(3)	94.2(1)	O(2)−V−N(4)	84.0(2)	81.16(9)
O(2)−V−N(3)	96.4(2)	93.2(1)	N(1)−V−N(4)	89.9(2)	89.6(1)
N(1)−V−N(3)	161.3(2)	161.0(1)	N(3)−V−N(4)	74.2(2)	75.3(1)
O(1)−V−N(2)	91.1(3)	95.3(1)	N(2)−V−N(4)	83.4(3)	80.5(1)
O(2)−V−N(2)	161.6(3)	158.5(1)			

equatorial plane of the distorted octahedron is defined by the monodentate ligand and three nitrogen atoms of the neutral chelate ligands while the oxo group and the remaining fourth nitrogen atom occupy the axial positions. As it has already been mentioned (see Experimental Section), the crystals of compounds $\mathbf{2}\cdot 1.2H_2O$ and $\mathbf{8}\cdot 0.5CH_2Cl_2$ showed poor diffraction quality, but we continued to collect data in order to determine the gross structure of them and to establish the cis orientation of the oxo moiety with respect to the monodentate ligands.

Focusing our discussion to the well characterized complex $\mathbf{6}\cdot CH_3OH\cdot 1.5H_2O$, we see that it compares well with the previously reported[25] oxovanadium(IV) compounds *cis*-$[V^{IV}O(OH)(bipy)_2]BF_4$ (**1**) and *cis*-$[V^{IV}O(OH)(phen)_2]BF_4\cdot H_2O$ (**1′**) [phen = 1,10-phenanthroline]. In particular, compounds $\mathbf{6}\cdot CH_3OH\cdot 1.5\ H_2O$, **1**, and **1′** present the same type of coordination about the oxovanadium(IV) center comprised of two N-donor neutral chelate agents and a monodentate ligand. Compound $\mathbf{6}\cdot CH_3OH\cdot 1.5H_2O$ contains the *cis*-$[V^{IV}O(OSO_3)]$ moiety, while compounds **1** and **1′** bear the *cis*-$[V^{IV}O(OH)]^+$ moiety. The main difference between them is that complex $\mathbf{6}\cdot CH_3OH\cdot 1.5H_2O$ is neutral, while compounds **1** and **1′** are cationic. The vanadium atom in $\mathbf{6}\cdot CH_3OH\cdot 1.5H_2O$ lies 0.33 Å above the equatorial plane toward the oxo moiety (0.25 and 0.24 Å in **1** and **1′**, respectively), and the V^{IV}═O axis is inclined at 83.9° with respect to the equatorial plane of the distorted octahedron (81.9° and 81.8° in **1** and **1′**, respecrtively). The two five membered chelate rings in the coordination sphere (i.e., V−N−C−C−N) are planar. The V═O bond of 1.584(2) Å lies in the range observed in analogous oxovanadium(IV) complexes (1.56−1.63 Å). On the contrary, in compounds **1** and **1′** the V═O bond length of ∼1.68 Å is well out of this range, a fact attributed to the competition of the hydroxy group with the O^{2-} group for the same vacant d_{xz} vanadium orbital.[25] The bipyridine ligands in $\mathbf{6}\cdot CH_3OH\cdot 1.5H_2O$, like in **1** and **1′**, are unsymmetrically ligated to the vanadium atom with the longer V−N distances V−N(2) = 2.142(3) Å and V−N(4) = 2.296(3) Å, being trans to the SO_4^{2-} and O^{2-} groups, respectively, and the shorter V−N distances [V−N(1) = 2.100(3) Å, V−N(3) = 2.117(3) Å] being trans to each other. The $V-O_{sulfate}$ bond length of 1.957(2) Å has been also observed in analogous compounds.[40] The O−V−O angle of the *cis*-$[V^{IV}O(OSO_3)]$ moiety in compound $\mathbf{6}\cdot CH_3OH\cdot 1.5H_2O$ is 105.0(1)°, a value close to the ∼107° observed in **1** and **1′** as well as in various 6-coordinate mononuclear vanadium(V) compounds containing the *cis*-$[V^VO_2]^+$ core.[24b]



$[V^{IV}O(bipy)_2]^{2+}$ $[V^{IV}OL_2]^{2+}$

Figure 5. Optimized geometries of the species $[V^{IV}O(bipy)_2]^{2+}$ and $[V^{IV}OL_2]^{2+}$ (hydrogens not shown).

Theoretical Calculations. The structure of $[V^{IV}O(bipy)_2]^{2+}$ species has never been solved experimentally or theoretically. It could adopt either a square pyramidal or a trigonal bipyramidal geometry. Thus, we have undertaken a theoretical study for both species $[V^{IV}O(bipy)_2]^{2+}$ and its model analogue $[V^{IV}OL_2]^{2+}$ in which the bipyridine ligand was replaced by the simple model ligand [HN═CH−CH═NH], L. The calculated under no symmetry constraints final optimized geometries are shown in Figure 5, while selected structural parameters are given in Table 6. The $[V^{IV}O(bipy)_2]^{2+}$ species adopts a trigonal bipyramidal structure of C_2 symmetry. The basal plane consists of the vanadium atom, the oxo, and the two nitrogen atoms, whereas the other two nitrogen atoms occupy the axial sites. The V═O and V−N bond lengths are unexceptional. All attempts to locate an even distorted square pyramidal structure were unsuccessful, as all optimizations gave the same structure regardless of the starting geometry. On the contrary, the geometry of the model complex, where no steric hindrance exists between the nonbulky ligands L, is square pyramidal with a C_{2v} symmetry. The vanadium atom lies out of the basal plane of the four nitrogen atoms by 0.546 Å toward the vanadium atom, and the V═O bond distance is a little shorter than that in $[V^{IV}O(bipy)_2]^{2+}$. No trigonal bipyramidal structure has been located for the model complex, even when the

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(40) Dong, Y.; Narla, R. K.; Sudbeck, E.; Uckum, F. M. *J. Inorg. Biochem.* **2000**, *78*, 321.

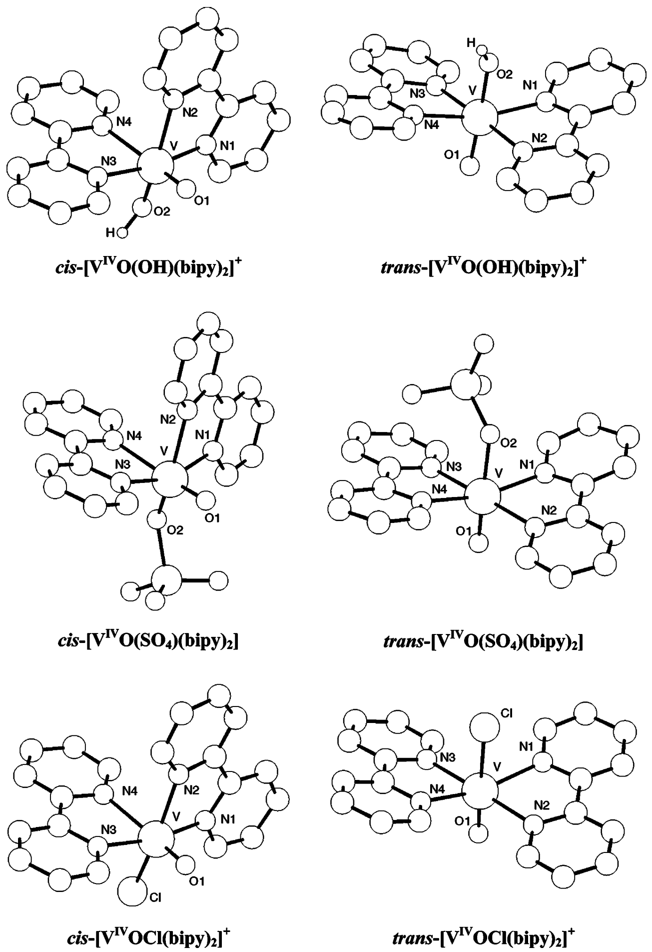
Table 6. Selected Bond Distances (Å) and Angles (deg) Calculated for the Species $[V^{IV}O(bipy)_2]^{2+}$ and $[V^{IV}OL_2]^{2+}$ [a]

	$[V^{IV}O(bipy)_2]^{2+}$	$[V^{IV}OL_2]^{2+}$
V−O(1)	1.577	1.565
V−N(1)	2.089	2.106
V−N(2)	2.101	2.106
V−N(3)	2.100	2.106
V−N(4)	2.089	2.106
O(1)−V−N(1)	119.6	105.0
O(1)−V−N(4)	119.6	105.0
N(1)−V−N(4)	120.8	150.0
N(3)−V−N(2)	171.0	150.0
N(2)−V−O(1)	94.5	105.0
N(2)−V−N(1)	78.3	76.7
N(2)−V−N(4)	97.2	95.5
N(3)−V−O(1)	94.5	105.0
N(3)−V−N(1)	97.2	95.5
N(3)−V−N(4)	78.3	76.7

[a] Numbering scheme as in Figure 5.

optimization was done under the C_2 symmetry constraint. Thus, we conclude that the trigonal bipyramidal geometry adopted by $[V^{IV}O(bipy)_2]^{2+}$ is mainly due to the existence of a strong hindrance between the hydrogen atoms of the two bipyridine ligands in a hypothetical square pyramidal geometry. Finally, it should be pointed out that $[V^{IV}O(bipy)_2]^{2+}$, being a +2 charged species, is a very electrophilic cation and a coordinatively unsaturated species, and should be very reactive toward donor solvent molecules or nucleophilic groups such as OH^-, SO_4^{2-}, or Cl^-. The sixth ligand, X, should approach the vanadium atom in the less crowded site, being the space between nitrogen atom and the oxo group in the basal plane of the trigonal bipyramid. Such a coordination apparently results in the 6-coordinate species $[V^{IV}OX(bipy)_2]^{n+}$, with a cis configuration of the $[V^{IV}OX]^{n+}$ fragment like these isolated in the present study.

All the 6-coordinate compounds under investigation, as well as the already known[24b] similar species $[V^{IV}OCl(bipy)_2]^+$, adopt the cis configuration for the $[V^{IV}OX]^{n+}$ fragment, whereas a trans configuration has been found for the related $[V^{IV}OCl(1\text{-vinylimidazole})_4]^+$ complex.[41] Thus, in order to explore the possibility of the existence of the trans configuration, the potential energy surface of the studied compounds has been searched out by DFT calculations. Full geometry optimizations starting from appropriate geometries were carried out without symmetry constraints for the species $[V^{IV}O(OH)(bipy)_2]^+$, $[V^{IV}O(OSO_3)(bipy)_2]$, and $[V^{IV}OCl(bipy)_2]^+$. In each case, two minima have been found corresponding to the cis and trans structures. The cis isomer has been found to be the global minimum, whereas the trans isomer has been found to be 45.56, 31.77, and 20.92 kJ/mol higher in energy for X = OH^-, SO_4^{2-}, and Cl^-, respectively. The calculated dipole moments of the cis isomers in the gas phase, being 6.5, 17.1, and 9.3 D for X = OH^-, SO_4^{2-}, and Cl^-, respectively, are considerably higher than those of the trans isomers being 2.7, 13.5, and 1.6 D for X = OH^-, SO_4^{2-}, and Cl^-, respectively. On the basis of the dipole moments, one expects that in solution and particularly in polar solvents the cis isomers would be significantly more stable than the trans ones. The calculated final optimized geometries of both isomers are shown in Figure 6, while selected structural parameters are given in Table 7. An overlay of the optimized cis structures, for *cis*-$[V^{IV}O(OH)(bipy)_2]^+$ and *cis*-$[V^{IV}O(OSO_3)(bipy)_2]$, and the experimental structures is shown in Figure 7. There is satisfactory agreement between the calculated cis structures and the experimental values of geometrical parameters for all species. At this point, it is worth noting that the calculated V═O bond distance of 1.690, 1.607, and 1.632 Å for *cis*-$[V^{IV}O(OH)(bipy)_2]^+$, *cis*-$[V^{IV}O(OSO_3)(bipy)_2]$ and *cis*-$[V^{IV}OCl(bipy)_2]^+$, respectively, is in excellent agreement with the experimental data 1.687(2), 1.584(2), and 1.619(4) Å, respectively. The elongation of the V═O bond has been attributed to the competition of the donor orbital of the hydroxy group, p_{OH}, with the donor orbital of the O^{2-} center, $p_{=O}$, for the same vacant d_{xz} vanadium orbital.[25] In the case of the sulfato complex the orientation of the SO_4^{2-} group in *cis*-$[V^{IV}O(SO_4)(bipy)_2]$ does not allow such a competition. This, along with the poor π-donor ability of the SO_4^{2-}group, results in a nonelongated V═O bond. Furthermore, a substantially smaller elongation of d(V═O) has been calculated in the case of *cis*-$[V^{IV}OCl(bipy)_2]^+$ (1.632 Å) due to the lower π-donor ability of the Cl^- ligand, in agreement with the findings of Brand et al. for the *cis*-$[V^{IV}OCl(bipy)_2]ClO_4$ complex (1.619 Å).[24b] The



cis-$[V^{IV}O(OH)(bipy)_2]^+$ *trans*-$[V^{IV}O(OH)(bipy)_2]^+$

cis-$[V^{IV}O(SO_4)(bipy)_2]$ *trans*-$[V^{IV}O(SO_4)(bipy)_2]$

cis-$[V^{IV}OCl(bipy)_2]^+$ *trans*-$[V^{IV}OCl(bipy)_2]^+$

Figure 6. Optimized geometries of the cis and trans isomers of the species $[V^{IV}O(OH)(bipy)_2]^+$, $[V^{IV}O(OSO_3)(bipy)_2]$, and $[V^{IV}OCl(bipy)_2]^+$ (hydrogens not shown).

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(41) Calviou, L. J.; Arber, J. M.; Collison, D.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1992**, 654.

Table 7. Selected Bond Distances (Å) and Angles (deg) Calculated for the Cis and Trans Isomers of the Species $[V^{IV}OX(bipy)_2]^{n+}$, X = OH^-, SO_4^{2-}, and Cl^- [a]

	OH^-, *cis*	OH^-, *trans*	SO_4^{2-}, *cis*	SO_4^{2-},*trans*	Cl^-,*cis*	Cl^-,*trans*
V−O(1)	1.690	1.625	1.607	1.638	1.632	1.608
V−X[b]	1.780	1.907	1.893	1.981	2.320	2.465
V−N(1)	2.126	2.149	2.106	2.160	2.137	2.233
V−N(2)	2.195	2.209	2.156	2.245	2.175	2.218
V−N(3)	2.121	2.218	2.065	2.182	2.120	2.233
V−N(4)	2.254	2.233	2.258	2.232	2.303	2.149
O(1)−V−X	108.9	174.1	107.5	88.8	105.5	177.0
O(1)−V−N(3)	89.6	90.8	92.2	90.3	91.4	88.0
X−V−N(3)	93.6	91.9	96.1	80.7	92.0	91.4
O(1)−V−N(1)	100.9	105.0	100.7	99.5	102.3	85.6
X−V−N(1)	87.2	79.4	86.0	71.1	86.7	81.7
N(3)−V−N(1)	168.6	105.2	158.9	106.2	163.0	104.4
O(1)−V−N(2)	90.6	87.0	91.7	164.3	92.9	89.6
X−V−N(2)	156.2	90.3	153.9	100.3	158.6	90.9
N(3)−V−N(2)	100.1	177.8	90.3	179.0	100.9	177.7
N(1)−V−N(2)	75.6	75.4	72.8	74.5	75.7	75.6
O(1)−V−N(4)	159.7	92.0	164.0	98.9	161.3	101.4
X−V−N(4)	85.1	83.6	85.7	91.5	84.6	81.2
N(3)−V−N(4)	74.5	75.6	75.0	76.4	73.6	75.4
N(1)−V−N(4)	94.2	162.9	89.0	161.4	92.4	162.9
N(2)−V−N(4)	80.1	104.4	79.0	103.3	79.4	105.2
X−H	0.976	0.976				
X−S			1.638	1.830		
V−X−H	128.5	136.9				
V−X−S			141.0	131.8		

[a] Numbering scheme as in Figure 6. [b] X = O(2) for $[V^{IV}O(OH)(bipy)_2]^+$ and $[V^{IV}O(OSO_3)(bipy)_2]$ and Cl^- for $[V^{IV}OCl(bipy)_2]^+$.

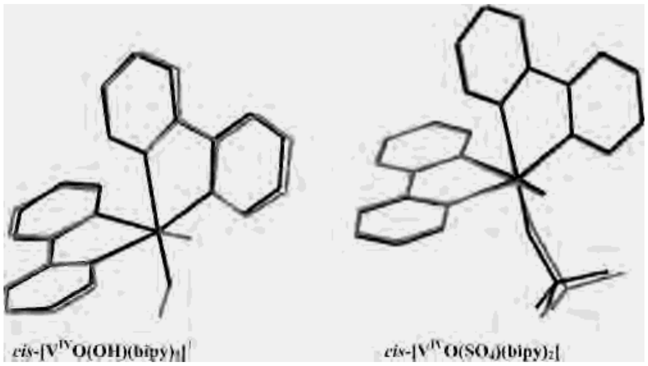

Figure 7. Overlay of the experimental (black) and calculated (gray) structures for *cis*-$[V^{IV}O(OH)(bipy)_2]^+$ and *cis*-$[V^{IV}O(OSO_3)(bipy)_2]$. Hydrogen atoms are not shown for clarity.

elongation of the V−N(4) and V−N(2) bonds is nicely attributed to the trans influence of the oxo and X^{n-} groups, respectively. There is also an inverse correlation between the V═O bond length and the V−N(4) bond length trans to it (see Table 9).

The structures of the calculated trans isomers deserve some comments. The V−X bond length is always elongated with respect to the cis structure due to the trans influence of the oxo group. The structures are highly distorted, and the nitrogen atoms in the basal plane deviate strongly from planarity. The two bipyridine ligands make an angle of 15.7°, 18.5°, and 15.8° for X = OH^-, SO_4^{2-}, and Cl^-, respectively. Thus, the steric hindrance between the bipyridine ligands seems to play a crucial role in the destabilization of the trans structures. In the case of the *trans*-$[V^{IV}OCl(1\text{-vinylimidazole})_4]^+$ species,[41] the imidazole ligands are inclined at 65° and 75° with respect to the N_4 plane. Thus, no steric destabilization exists, and the species adopts the trans configuration.

To further elucidate the relative stability of the cis configuration of the $[V^{IV}OX]^{n+}$ fragment in the studied compounds, we have also optimized the cis and trans structures of the model complexes $[V^{IV}OXL_2]^{n+}$, X = OH^-, SO_4^{2-}, and Cl^-. In the model species no steric hindrance exists between the ligands L in the trans isomers. The size of these model species allowed us to calculate the Hessian in all cases. Both isomers are minima in the potential surface of the molecule, as no imaginary frequencies have been calculated. The calculated final optimized geometries of both isomers are shown in Figure S1, while selected structural parameters are given in Table S1. The trans structures are highly symmetric due to the lack of steric hindrance and adopt a nearly C_s symmetry for X = OH^- and SO_4^{2-} and C_{2v} symmetry for X = Cl^-, whereas the vanadium atom lies out of the basal plane of the four nitrogen atoms in the direction of the oxo-group by 0.035 Å, 0.189 Å, and 0.214 Å for X = OH^-, SO_4^{2-}, and Cl^-, respectively. As in the case of the actual compounds, the cis isomer of the model species has been found to be the global minimum for all X groups, whereas the trans isomer has been found to be 25.92, 10.87, and 1.67 kJ/mol higher in energy for X = OH^-, SO_4^{2-}, and Cl^-, respectively. The much lower cis−trans energy difference in these $[V^{IV}OXL_2]^{n+}$ species, compared to that in the actual compounds, is traced back to an intrinsic preference of the complexes for the cis geometry. This preference should be caused by electronic phenomena stabilizing the cis or destabilizing the trans structures, due to differences between the two geometries concerning the interactions of the ligand and metal orbitals. In the trans configuration, the filled orbitals of the σ- and π-donor oxo and X ligands compete for the same d-orbitals of the metal, a fact that apparently leads to destabilization. In the cis configuration, such a competition in both the σ- and

Table 8. EPR Parameters[a] of a Few Characteristic Oxovanadium(IV) Compounds of the Present Study

					$\times 10^{-4}$ cm^{-1}				
compd	solvent	g_x	g_y	g_z	A_x	A_y	A_z	donor set	ref
1	CH_3CN	1.981	1.978	1.944	53	64	163	$N_3O_{OH^-}$	25
	H_2O[b]	1.980	1.977	1.943	53	63	163		this work
	powder			1.942			163		this work
5	CH_3CN	1.981	1.981	1.945	53	63	163	$N_3O_{OH^-}$	this work
	H_2O[b]	1.981	1.980	1.945	53	63	163		this work
6$\cdot CH_3OH\cdot 1.5H_2O$	CH_2Cl_2	1.980	1.980	1.945	65	65	162	$N_3O_{SO_4^{2-}}$	this work
7	CH_2Cl_2	1.988	1.988	1.942	52	52	164	N_3Cl	this work
	CH_3OH	1.9850	1.9820	1.9581	53.80	54.48	156.58	$N_3O_{CH_3O^-}$	24b
	CH_2Cl_2/CH_3OH (1:1)	1.982	1.982	1.958	55	55	157	$N_3O_{CH_3O^-}$	this work
9	CH_2Cl_2	1.988	1.982	1.942	52	52	164	N_3F	this work
10	CH_2Cl_2	1.988	1.988	1.942	52	52	164	N_3F	this work
11	CH_2Cl_2	1.988	1.988	1.942	52	52	164	N_3F	this work

[a] Errors: g values $\pm$ 0.003; hyperfine coupling constants $\pm 0.8 \times 10^{-4}$ cm^{-1}. [b] In water, in addition to **1** and **5**, there was another species with $g_{x,y} = 1.981$, $g_z = 1.936$, $A_{x,y} = 64$, and $A_z = 175 \times 10^{-4}$ cm^{-1} in about 20%. It is worth noting that the 1,10-phenanthroline analogues of **1** and **5**, i.e., *cis*-$[VO(OH)(phen)_2]BF_4\cdot H_2O$ (**1′**) and *cis*-$[VO(OH)(phen)_2]ClO_4$ (**5′**), gave only signals for **1′** and **5′** with exactly the same EPR parameters reported in Table 8 for **1** and **5**, respectively. This is might be due to the rigidity of the phen ligand.

Table 9. Comparison of d(V=O), d(V−X) (X = OH^-, SO_4^{2-}, Cl^-), and d(V−N) [Å] trans to O^{2-} and X for All Structurally Characterized Oxovanadium(IV) Compounds of the General Formula *cis*-$[V^{IV}OX(L_{NN})_2]^{+/0}$ [a]

compd	d(V=O)	d(V−X)	d(V−N)[b]	d(V−N)[c]	X	av(V−N)[d]	trans influence of X and O^{2-},[e] to trans N atom (Å)	ref
1	1.687(2)	1.761(2)	2.247(3)	2.175(3)	OH^-	2.113 (3)	0.062(3) [0.134(3)]	25
2$\cdot 1.2H_2O$	1.659(6)	1.785(5)	2.261(6)	2.179(6)	OH^-	2.111 (6)	0.068(6) [0.150(6)]	this work
1′	1.677(3)	1.778(2)	2.246(3)	2.173(3)	OH^-	2.112(3)	0.061(3) [0.134(3)]	25
6$\cdot CH_3OH\cdot 1.5H_2O$	1.584(2)	1.957(2)	2.296(3)	2.142(3)	SO_4^{2-}	2.109 (3)	0.033(3) [0.187(3)]	this work
cis-$[V^{IV}O(SO_4)(phen)_2]$	1.584(5)	1.960(5)	2.325(6)	2.135(6)	SO_4^{2-}	2.119(6)	0.017(6) [0.206(6)]	40
cis-$[V^{IV}OCl(bipy)_2]ClO_4$	1.619(4)	2.328(2)	2.289(5)	2.127(6)	Cl^-	2.137 (5)	∼0.0[0.152(5)]	24b

[a] L_{NN} is bipy or phen. [b] Nitrogen atom trans to O^{2-}. [c] Nitrogen atom trans to X. [d] Average V−N bond distance of the two trans to each other equatorial nitrogen atoms. [e] Values in square brackets.

π-systems does not exist, except in the case of the π-system of the *cis*-$[V^{IV}O(OH)(bipy)_2]^+$ complex. Furthermore, the cis configuration of the $[V^{IV}OX]^{0/+}$ sructural unit allows the interaction of the π^*-acceptor orbitals of bipyridine and the π-donor orbitals of the oxo or X ligands with the same metal d-orbital, leading to a X → M → N or O → M → N “push pull” interaction, which is known to stabilize the compound.[42] Finally, comparison of the corresponding cis−trans energy difference of the model in comparison with the actual species reveals that there is an almost constant increment of 19.64, 20.90, and 19.25 kJ/mol for X = OH^-, SO_4^{2-}, and Cl^-, respectively, which should be safely attributed to the aforementioned destabilization of the trans structures of the actual complexes due to steric hindrance.

Magnetism and Electron Paramagnetic Resonance Spectra. The magnetic moments of compounds **1**−**11** are in the range 1.66−1.75 μ_B, at 298 K in accord with the spin-only value expected, for d^1, $S = {}^1/_2$ systems. The EPR parameters (**A** and **g** tensors) of a few characteristic oxovanadium(IV) compounds of the present study were determined by computer simulation of the experimental EPR spectra and are reported in Table 8. The CW EPR spectrum of **1** in acetonitrile is shown in Figure 8.

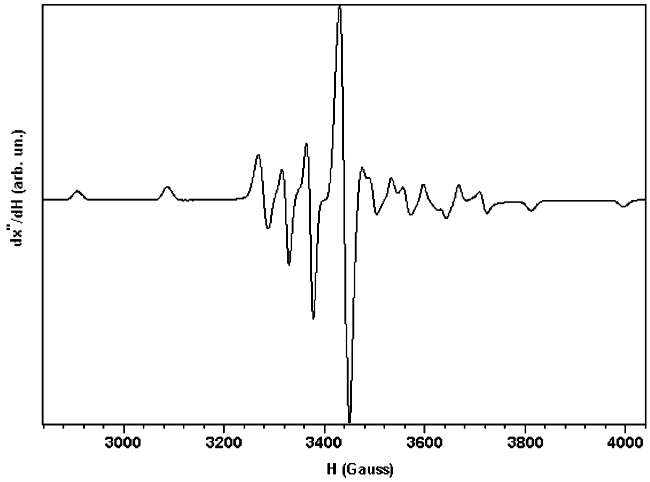

Figure 8. Continuous wave EPR spectrum of **1** in CH_3CN. Experimental conditions: temperature 20 K, microwave frequency 9.256 GHz, microwave power attenuation 18 dB, modulation amplitude 12.5 G, modulation frequency 100 kHz.

Figure 9 displays a correlation plot between A_z and g_z values for a series of known oxovanadium(IV) compounds with various equatorial donor atom sets.[11d,43] Addition of the g_z and A_z values for **1**, **6**$\cdot CH_3OH\cdot 1.5H_2O$, and **7** to this plot, with donor sets $N_3O_{OH^-}$, $N_3O_{SO_4^{2-}}$, and N_3Cl, respectively, reveals that their points are very close to each other and to the reference $(V^{IV}O)N_4$ {*trans*-$[V^{IV}OCl(1\text{-vinylimidazole})_4]Cl$}[41] compound, which has been structurally characterized. This fact explains why the research groups who studied the system $V^{IV}O^{2+}$/bipy in solution misleadingly assigned the

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(42) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem*. **1994**, *33*, 1476.

(43) (a) Tasiopoulos, J. A.; Troganis, A. N.; Evangelou, A.; Raptopoulou, P. C.; Terzis, A.; Deligiannakis, Y.; Kabanos, T. A. *Chem. Eur. J.* **1999**, *5*, 910. (b) Tolis, J. E.; Teberekidis, I. V.; Raptopoulou, P. C.; Terzis, A.; Sigalas, P. M.; Deligiannakis, Y.; Kabanos, T. A. *Chem. Eur. J.* **2001**, *7*, 2698.

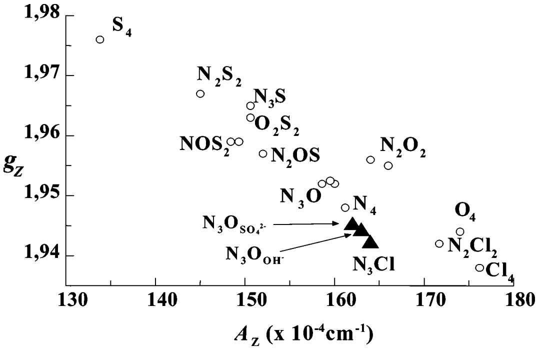

Figure 9. Correlation plot between A_z vs g_z values for a series of known oxovanadium(IV) compounds with various equatorial-donor-atom sets and for compounds (▲) **1**, **6**·CH_3OH·1.5H_2O, and **7**.

EPR spectra of it to $[V^{IV}O(bipy)_2]^{2+}$ species, irrespective of the conditions used. From the data of the present study, it is crystal clear that the $V^{IV}O^{2+}$ cation in aqueous solution without a coordinating counterion present (e.g., Cl^-, SO_4^{2-}) and in the presence of 2 equiv of bipy gives an EPR signal which is attributed to the species *cis*-$[V^{IV}O(OH)(bipy)_2]^+$, while in the case of the $V^{IV}O^{2+}$/bipy species in the presence of coordinating counterions (e.g., Cl^-, SO_4^{2-}), in high concentrations (~0.2 M), the EPR data rather correspond to the *cis*-$[V^{IV}OX(bipy)_2]^{n+}$ species ($X = Cl^-$, SO_4^{2-}).[24a,c]

Application of the additivity relationship[11d] for compound **7** gives a calculated A_z value of 165.6 × 10^{-4} cm^{-1}, with proposed equatorial coordination (3N$_{pyr}$, 1Cl$^-$), which deviates substantially from the experimental A_z value in methanol[24b] or dichloromethane/methanol (1:1), being ≈157 × 10^{-4} cm^{-1} (Table 8). A reasonable explanation for this discrepancy is that an alcoholysis occurs for the species *cis*-$[V^{IV}OCl(bipy)_2]^+$ in these solvents and the measured EPR parameters correspond to the species *cis*-$[V^{IV}O(OR)(bipy)_2]^+$. Application of the additivity relationship for the latter species gives a calculated A_z value of 156.8 × 10^{-4} cm^{-1}, with proposed equatorial coordination (3N$_{pyr}$, 1RO$^-$), which is almost identical to the experimental A_z value of 157 × 10^{-4} cm^{-1}. When dichloromethane was used as a solvent for compound **7**, the experimental A_z value was 164 × 10^{-4} cm^{-1}, that is, very close to the calculated A_z value of 165.6 × 10^{-4} cm^{-1} reported above.

The EPR parameters of compounds **9**−**11** in CH_2Cl_2 are identical to those of compound **7**, i.e., *cis*-$[V^{IV}OCl(bipy)_2]$-Cl, in CH_2Cl_2 as well (Table 8). This fact seems odd, but taking into account the conductivity of **9**−**11** in CH_2Cl_2 (Table 4), it is obvious that they behave as 1:1 electrolytes which means that one BF_4^- or one SbF_6^- is ligated to the metal through its fluorine atom (see Scheme 1). The proposed *cis*-$[V^{IV}O(F...)]^+$ structure for **9**−**11**, based on conductivity measurements, gives an explanation for the almost identical EPR parameters of compounds **9**, **10**, and **11** with those of **7**.

A comparison of *d*(V═O), *d*(V−X) [X = OH^-, SO_4^{2-}, Cl^-], and *d*(V−N) trans to O^{2-} and X for the oxovanadium(IV) compounds of the general formula *cis*-$[VO(X)L_{NN}]^{+/0}$ (L_{NN} = bipy or phen) is reported in Table 9. From the data of Table 9, it is evident that the O^{2-} group exerts the strongest trans influence, expressed as the elongation of *d*(V−N) in comparison with the average *d*(V−N) of the two trans equatorial nitrogen atoms, on the nitrogen atoms, being in the range ~0.13−0.21 Å. The hydroxy group exerts also a strong trans influence on the nitrogen atom, being in the range 0.06−0.07 Å. It is obvious that the chlorine atom does not exert any trans influnce on the nitrogen atom, while it is rather difficult to comment upon the trans influence of the sulfate (-O) group since the two entries in Table 9 do not give consistent results. The A_z contribution of the aromatic nitrogen atom in the $V^{IV}O^{2+}$ species has been worked out with an average *d*(V−N) of 2.10 Å and not 2.17, 2.18, or 2.14 Å. The present structural and spectroscopic data for the oxovanadium(IV) compounds studied here indicate that the A_z value of ^{51}V, measured by CW EPR spectroscopy, can be invariant despite the differences in the geometrical disposition of the ligand donor atoms. In this context, it is of relevance to point out that the A_z (^{51}V) value in these compounds cannot distinguish the details of the geometrical disposition of the ligated nitrogens to vanadium. On the other hand, the individual hyperfine couplings (A_{iso})[44] of the ligated nuclei, for example ^{14}N, are sensitive to the geometrical disposition of the donor atoms. For example, the ESEEM[25] data for compound **1** show that the A_{iso} value for the two equivalent nitrogen atoms N(1) and N(3), oriented trans to each other, is 4.6 MHz, while the A_{iso}(^{14}N) value of the N(2) atom, trans to OH^- group, is 6.6 MHz.

Conclusions

Two classes of monomeric oxovanadium(IV) compounds, containing bipy or 4,4′-disubstituted bipy (L_{NN}), of general formulas *cis*-$[V^{IV}OX(L_{NN})_2]^{+/0}$ ($X = OH^-$, SO_4^{2-}, Cl^-) and *cis*-$[V^{IV}OY(L_{NN})_2]Y$ ($Y = BF_4^-$, SbF_6^-) were synthesized by treating $[V^{IV}OCl_2(THF)_2]$ or $V^{IV}OSO_4$·5H_2O in either H_2O or CH_2Cl_2 with 2 equiv of $AgBF_4$ or $AgSbF_6$ or 1 equiv of $Ba(ClO_4)_2$ and 2 equiv of L_{NN}. With the exception of the two compounds **6**·CH_3OH·1.5H_2O and **7** containing the *cis*-$[V^{IV}O(OSO_3)]$ and *cis*-$[V^{IV}OCl]^+$ cores, respectively, which were synthesized by reacting $V^{IV}OSO_4$·5H_2O or $[V^{IV}OCl_2(THF)_2]$ with 2 equiv of the chelate ligand L_{NN}. The compounds **1**−**5** constitute rare examples of $V^{IV}O^{2+}$ compounds containing the *cis*-$[V^{IV}O(OH)]^+$ core isolated and structurally characterized (compounds **1** and **2**·1.2H_2O).

Theoretical calculations for the $[V^{IV}O(bipy)_2]^{2+}$ species revealed that in the gas phase it would have a trigonal bipyramidal geometry. The $[V^{IV}O(bipy)_2]^{2+}$ cation, which is a strong Lewis acid and a coordinatively unsaturated species, should be very reactive toward donor solvent molecules or anionic groups such as OH^-, SO_4^{2-}, Cl^-, etc. The ligation of a sixth ligand to $[V^{IV}O(bipy)_2]^{2+}$ cation results in a 6-coordinate species $[V^{IV}OX(bipy)_2]^{n+}$, with a cis configuration of the $[V^{IV}OX]^{n+}$ fragment. The cis configuration in the latter species, according to the theoretical study, is a result of steric hindrance between the bipyridine ligands as well as of electronic phenomena. Thus, the theory predicts

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[44] Chasteen, N. D.; Snetsinger, P. A. ESEEM and ENDOR Spectoscopy. In *Physical Methods in Bioinorganic Chemistry: Spectroscopy and Magnetism*; Que, L., Jr., Ed.; University Science Books: Sausalito, CA, 2000; pp 187−231.

that in water, without the presence of any coordinating ligand (Cl^-, SO_4^{2-}, etc.), the *cis*-$[V^{IV}O(H_2O)(bipy)_2]^{2+}$ or *cis*-$[V^{IV}O(OH)(bipy)_2]^+$ complexes could only exist, and this is in excellent agreement with our experimental data.

CW EPR data for some characteristic oxovanadium(IV) compounds of the present study of the general formula *cis*-$[V^{IV}OX(L_{NN})_2]^{+/0}$ ($X = OH^-$, Cl^-, F^-, SO_4^{2-}) revealed that their ^{51}V hyperfine coupling constants A_z are very similar, almost identical. Moreover, the A_z values of these compounds are very close to the A_z values reported in the literature for the aqueous $V^{IV}O^{2+}$/bipy system with or without the presence of coordinating ligands (i.e., Cl^-, SO_4^{2-}). This fact explains why all the research groups who did EPR measurements in the $V^{IV}O^{2+}$/bipy system assigned their data to the species $[V^{IV}O(bipy)_2]^{2+}$, which in water does not exist. The A_z (^{51}V) values may serve as reference values, e.g., for the prediction of the equatorial donor atom types in oxovanadium(IV) compounds. In light of the present findings, however, it is of importance to note that the use of A_z (^{51}V) values as diagnostic tool should be done with care. More specifically, the mere use of A_z (^{51}V) values from model compounds which have not been isolated nor structurally characterized may be not sufficient to define the equatorial coordination sphere. In the same context, it is of relevance to point out that advanced EPR techniques such as ESEEM and 2D-HYSCORE offer a reliable spectroscopic tool for the elucidation of the equatorial donor atoms.

Supporting Information Available: Additional table and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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