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Article

Unexpected Synthesis of an Unsymmetrical μ-Oxido Divanadium(V) Compound through a Reductive Cleavage of a N−O Bond and Cleavage-Hydrolysis of a C−N Bond of an N,N-Disubstituted Bis-(hydroxylamino) Ligand

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Reaction of the N,N-disubstituted bis-(hydroxylamino) ligand 2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazine, H_2bihyat, with $V^{IV}OSO_4 \cdot 5H_2O$ in water for 6 h followed by the addition of methyl alcohol resulted in the isolation of the unsymmetrical μ-oxido divanadium(V) compound $[V^V{}_2O_2(\mu_2\text{-}O)(\text{bihyat})(\text{hyta})(\text{hyto})] \cdot 3H_2O$ (**1**$\cdot 3H_2O$) and of the methylhydroxylamido derivative $[V^VO(\text{bihyat})(CH_3NHO)] \cdot H_2O$ (**2**$\cdot H_2O$). The N,N-disubstituted mono(hydroxylamino) ligands Hhyta, Hhyto, and CH_3NHOH were formed by the decomposition of the ligand H_2bihyat in the presence of vanadium. The structures of compounds **1**$\cdot 3H_2O$ and **2**$\cdot H_2O$ were determined by X-ray crystallography. The structure of **1**$\cdot 3H_2O$ consists of one five-coordinate vanadium(V) atom and one six-coordinate vanadium(V) atom bridged by an oxido group and ligated to a tridentate bihyat^{2-} and two bidentate hyta$^-$ and hyto$^-$ ligands, respectively. The two terminal oxido groups in **1**$\cdot 3H_2O$ are syn-directed, lying on the same side of the V−O−V plane. The coordination environment of the vanadium atom in **2**$\cdot H_2O$ approximates to a highly distorted pentagonal pyramid with the oxido ligand occupying the apical position. Compounds **1**$\cdot 3H_2O$ and **2**$\cdot H_2O$ were studied by multinuclear NMR (^{1}H, ^{13}C, and ^{51}V) to elucidate their solution structures. The ^{51}V NMR of **1**$\cdot 3H_2O$ in anhydrous CD_2Cl_2 gave two signals at −199 and −508 ppm, which were assigned to the five- and six-coordinate vanadium(V) atoms, respectively. The resonance of the five-coordinate vanadium nucleus, in a field much lower than that expected from Rehder's [*Inorg. Chem.,* **1988**, *27*, 584−587] referencing scale, was attributed to the low-energy ligand-to-metal charge transfer transition at 605 nm [$\varepsilon_M = 5050\ M^{-1}\ cm^{-1}$] of **1**$\cdot 3H_2O$ according to Pecoraro et al. [*J. Am. Chem. Soc.,* **1992**, *114*, 9925−9933]. Electrospray ionization−mass spectrometry studies were used to follow the decomposition products of H_2bihyat in the presence of vanadium.

Introduction

Vanadium is a bioessential element that is found in two enzyme families, the vanadate-dependent haloperoxidases[1,2] and vanadium−nitrogenases.[3] In addition, vanadium is present in remarkably high concentrations in sea squirts[3a,b] (and fan worms)[3a,b] and in certain mushrooms of the genus *Amanita*.[4] The naturally occurring vanadium compound in

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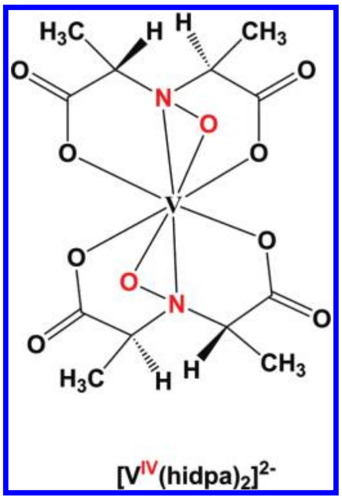
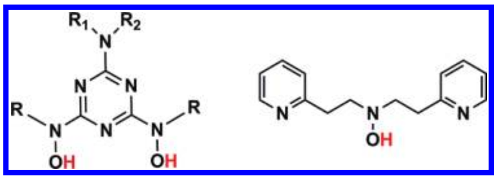
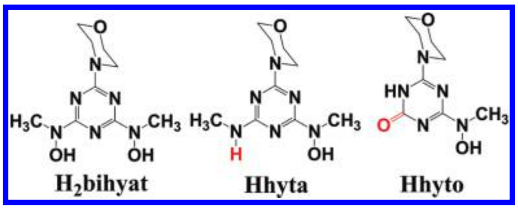
Scheme 1



Scheme 2



Scheme 3. Molecular Structures of the Ligands H_2bihyat, Hhyta, and Hhyto



mushrooms is called amavadine.[5] In amavadine, the chelating *N,N′*-disubstituted hydroxylamide ligand N-hydroxy-*a*,*a′*-iminodipropionate, hidpa^{3-}, forms a nonoxido−vanadium(IV) complex, $[V^{IV}(hidpa)_2]^{2-}$ (Scheme 1). The anion hidpa^{3-} is unique because it is the only known naturally occurring ligand that has a higher affinity for vanadium than any other metal.[6] The $[V^{IV}(hidpa)_2]^{2-}$ species has great hydrolytic stability[7] and also exhibits reversible one-electron redox properties.[8] In addition, amavadine is an excellent catalyst for various transformations,[9] such as CH_4 to CH_3COOH and so forth. It has been proposed that amavadine serves as an electron transfer agent in the mushroom,[3a,b] though a few other hypotheses have been put forward.[3a,b] In any case, the role of amavadine is still poorly understood. Although the coordination chemistry of unmodified hydroxylamine and its alkyl-substituted derivatives with vanadium[10] and molybdenum[11] was extensively studied, the ligation of vanadium and molybdenum with chelating hydroxylamino ["chehyl"] ligands remains surprisingly unexplored. A literature survey revealed that the metal-binding properties of only two chelating N,N-disubstituted hydroxylamino ligands, except for H_3hidpa,[5] have been very recently reported[12,13] (Scheme 2). These facts inspired us to embark on an effort to further explore the vanadium−"chehyl" chemistry.

In the present study, the synthesis and structural and physicochemical characterization of a rare example[14] of an unsymmetrical *μ*-oxido divanadium(V) compound $[V^V_2O_2(\mu_2\text{-}O)(bihyat)(hyta)(hyto)]\cdot 3H_2O$ (**1**$\cdot 3H_2O$) with the "chehyl" ligands H_2bihyat, Hhyta,[15] and Hhyto[15] (Scheme 3) are reported. The ligands Hhyta and Hhyto (Scheme 3) resulted from the reductive cleavage of a N−O bond and cleavage-hydrolysis of a C−N bond of H_2bihyat, in the presence of vanadium, respectively. In addition, the synthesis and structural and physicochemical characterization of the (N-methylhydroxylamido-O,N) oxidovanadium(V) derivative $[V^VO(bihyat)(CH_3NHO)]\cdot H_2O$ (**2**$\cdot H_2O$) are also reported.

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(15) Systematic nomenclature of the ligands Hhyta and Hhyto according to IUPAC rules is Hhyta, 4-[hydroxy(methyl)amino]-N-methyl-6-morpholino-4-yl-1,3,5-triazin-2-amine; Hhyto, [4-hydroxy(methyl)amino]-6-morpholino-4-yl-triazin-2(1H)-one.

Experimental Section

Materials. $V^{IV}OSO_4 \cdot 5H_2O$ (96%), $NaV^{V}O_3$ (99.9%), and N-methylhydroxylamine hydrochloride were purchased from Merck, Aldrich, and Fluka, respectively, and used without any further purification. CD_2Cl_2 was dried over CaH_2, and it was distilled just prior to its use. The ligand H_2bihyat was prepared by the literature procedure.[12d] C, H, and N analyses were conducted by the microanalytical service of the Department of Chemistry, University of Lisboa. Vanadium was determined gravimetrically as vanadium pentoxide.

μ_2-Oxido-{2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazinato-O,O,N} Oxidovanadium(V)-{4-[hydroxy(methyl)amino]-N-methyl−6-morpholino-4-yl-1,3,5-triazin-2-aminato-O,N}-{[4-hydroxyl(methyl)amino]-6-morpholino-4-yl-triazin-2(1H)-onato-O,N} Oxidovanadium(V), $[V_2^{V}O_2(\mu_2\text{-}O)$(bihyat)(hyta)(hyto)$] \cdot 3H_2O$ ($1 \cdot 3H_2O$). Solid H_2bihyat (0.150 g, 0.60 mmol) was added in one portion to a stirred solution of $V^{IV}OSO_4 \cdot 5H_2O$ (0.150 g, 0.60 mmol) in deoxygenated water (30 mL) at room temperature (~20 °C). Upon addition of the ligand, the blue color of the solution turned to brown, and when the whole quantity of it was dissolved, its color changed to yellow-brown. The reaction mixture was stirred for 6 h at room temperature (~20 °C), and then it was filtered. Methyl alcohol (30 mL) was then carefully layered on the top of the filtrate, and the reaction mixture was allowed to sit for ~2 weeks at room temperature (~20 °C) to afford black crystals of $\mathbf{1} \cdot 3H_2O$ and yellow crystals of $\mathbf{2} \cdot H_2O$ suitable for X-ray structure analysis. The colorless solution was decanted, and the crystals were washed with methyl alcohol (3 × 1 mL), where $\mathbf{2} \cdot H_2O$ is very soluble, to get 0.045 g of $\mathbf{1} \cdot 3H_2O$. Yield, 16% (based on vanadium). Absorption spectrum (anhydrous dichloromethane): λ_{max} (ε_M, $M^{-1}cm^{-1}$) 605 nm (5050), 270 nm (sh, 31 000). Solid state: λ_{max} (nm) 608, 275 (sh), 238, 219. IR (KBr) 3430 (m), 2960 (w), 2926 (m), 2894 (vs), 1700 (m), 1578 (vs), 1541 (vs), 1501 (m), 1435 (m), 1386 (m), 1312 (m), 1272 (s), 1228 (w), 1195 (w), 1112 (s), 1021 (m), 960 (s), 862 (w), 802 (s), 691 (w), 667 (w), 608 (m), 545 (w), 501(w), 421 (w). Elem anal. calcd (%) for $C_{26}H_{47}N_{17}O_{14}V_2$ (923.69): C, 33.81; H, 5.13; N, 25.78; V, 11.03. Found: C, 33.60; H, 5.09; N, 25.63, V, 10.95.

{2,6-Bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazinato-O,O,N}(methylhydroxylamido-N,O) Oxidovanadium(V), $[V^{V}O$(bihyat)(methy)$] \cdot H_2O$ ($2 \cdot H_2O$). Method A. Compound $\mathbf{2} \cdot H_2O$ was prepared as described above for the synthesis of $\mathbf{1} \cdot 3H_2O$ except that (i) $V^{IV}OSO_4 \cdot 5H_2O$ (0.150 g, 0.60 mmol) was dissolved in only 15 mL of water instead of 30 mL, (ii) the solvent of the reaction was only water, and (iii) the molar ratio of $V^{IV}OSO_4 \cdot 5H_2O$:H_2bihyat was 1:2. Upon dissolution of the ligand H_2bihyat, a yellow precipitate was formed. After an additional 3 h of stirring, the precipitate was filtered off, washed with 1.0 mL of water, and dried in vacuo. Yield, 0.120 g (52% based on vanadium).

Method B. Solid H_2bihyat (0.100 g, 0.40 mmol) was added in one portion to a stirred aqueous solution of $NaV^{V}O_3$ (0.048 g, 0.40 mmol) in deoxygenated water (3 mL) at room temperature (~20 °C). Upon dissolution of the ligand, the colorless solution of $NaV^{V}O_3$ turned to orange. The pH of the solution was 6.5. Methylhydroxylamine hydrochloride (0.033 g, 0.40 mmol) was added to this solution, and its color immediately changed to red-orange and after 10 min of stirring to yellow, followed by the precipitation of $\mathbf{2} \cdot H_2O$ as a yellow solid. The pH of the solution dropped to 5. After an additional 30 min of stirring, the precipitate was filtered off, washed with 1 mL of water, and dried in vacuo. Yield, 0.104 g (70% based on vanadium). Absorption spectrum (dichloromethane): λ_{max} (ε_M, M^{-1} cm^{-1}) 370 nm (1262), 244 nm (33 500). Solid state: λ_{max} (nm) 367, 222. IR (KBr): 3416 (m), 3094 (m), 2966 (w), 2922 (m), 2896 (w), 1653 (s), 1558 (vs), 1502 (vs), 1461 (w), 1436 (m), 1398 (m), 1319 (m), 1286 (m), 1200 (w), 1166 (w), 1098 (s), 1061 (m), 1023 (m), 974 (s), 942 (m), 848 (w), 818 (m), 764 (m), 702 (w), 682 (w), 641 (w), 611 (w), 584 (w), 550 (w), 523 (w), 477 (w), 436 (w). Elem anal. calcd (%) for $C_{10}H_{20}N_7O_6V$ (385.27): C, 31.18; H, 5.23; N, 25.45; V, 13.22. Found: C, 30.92; H, 5.18; N, 25.32; V, 14,19.

Table 1. Summary of X-Ray Crystallographic and Experimental Data for the Compounds $\mathbf{1} \cdot 3H_2O$ and $\mathbf{2} \cdot H_2O$

parameter	$\mathbf{1} \cdot 3H_2O$	$\mathbf{2} \cdot H_2O$
composition	$C_{26}H_{47}N_{17}O_{14}V_2$	$C_{10}H_{20}N_7O_6V$
fw	923.69	385.27
cryst syst	orthorhombic	triclinic
space group	*Pna*21	$P\bar{1}$
a, Å	14.8530(12)	7.8156(6)
b, Å	16.1914(13)	8.8133(8)
c, Å	16.2365(13)	12.7313(10)
α, deg	90.00	102.554(7)
β, deg	90.00	92.762(6)
γ, deg	90.00	113.268(8)
V, $Å^3$	3904.7(5)	777.52(13)
D_{calcd}, Mg m^{-3}	1.571	1.646
temp, K	100(1)	100(1)
λ (Mo Kα), Å	0.71073	0.71073
Z	4	2
F(000)	1920	400
θ range for data collection (deg)	2.24−26.00	2.60−25.00
μ mm^{-1}	0.565	0.684
reflns collected/unique	23217/6351	5799/2692
R_{int}/GOF on F^2	0.0921/0.885	0.0462/1.229
data/restraints/params	6351/157/537	2692/0/220
R1(F_o), wR2(F_o) [$I \geq 2\sigma(I)$]	0.0400, 0.0533	0.0497, 0.1187
R1(F_o^2), wR2(F_o^2) (all data)	0.0964, 0.0642	0.0712, 0.1284

X-Ray Structure Determination. Intensity data for the crystals of $\mathbf{1} \cdot 3H_2O$ and $\mathbf{2} \cdot H_2O$ were collected at 100(1) K on a KUMA KM4CCD four-circle diffractometer with a CCD detector,[16a] using graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). Cell parameters were determined by a least-squares fit of 4653 ($\mathbf{1} \cdot 3H_2O$) and 2939 ($\mathbf{2} \cdot H_2O$) reflections taken from the whole data sets. All data were corrected for Lorentz-polarization effects and absorption.[16] The structures were solved with direct methods with SHELXS97 and refined by full-matrix least-squares procedures on F^2 with SHELXL97.[16b] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined via the "riding model" with isotropic thermal parameters fixed at 1.2 (1.3 for CH_3 groups) times the U_{eq} value of the appropriate carrier atom. Significant crystal data for the compounds $\mathbf{1} \cdot 3H_2O$ and $\mathbf{2} \cdot H_2O$ are given in Table 1.

NMR Spectroscopy. NMR experiments were performed on a Bruker AV-500 spectrometer operating at 500.13 MHz, 125.77 MHz, and 131.49 MHz for ^1H, ^{13}C, and ^{51}V nuclei, respectively. Routine parameters were used for ^1H and ^{13}C data acquisition and processing. The ^{51}V spectra were recorded using a $\pi/2$ excitation pulse, spectral width of 119 047 Hz, acquisition time of 0.69 s, relaxation delay of 0.1 s, and 2000−8000 scans. The ^{51}V chemical shifts were obtained using an external reference of $V^{V}OCl_3$ (resonating at 0 ppm). The 2D acquisition parameters for $^1H-^1H$ DQF-COSY experiments were as follows: spectral width, 6009 Hz; acquisition time, 0.17 s,; relaxation delay, 2; and two scans were acquired for each of 768 increments. $^1H-^{13}C$ HSQC experiments were acquired with a spectral width of 4251 Hz in the *F*2 (^1H) dimension and 20 833 Hz in the *F*1 (^{13}C) dimension; acquisition time was 0.24 s, relaxation delay was 1.5 s, and there were 80 scans acquired for 256 increments. When low-temperature NMR experiments were performed, the sample in the spectrometer was equilibrated for at least 10 min prior to data acquisition. NMR data were processed using Topspin 1.3 NMR (Bruker) software. The samples were prepared by

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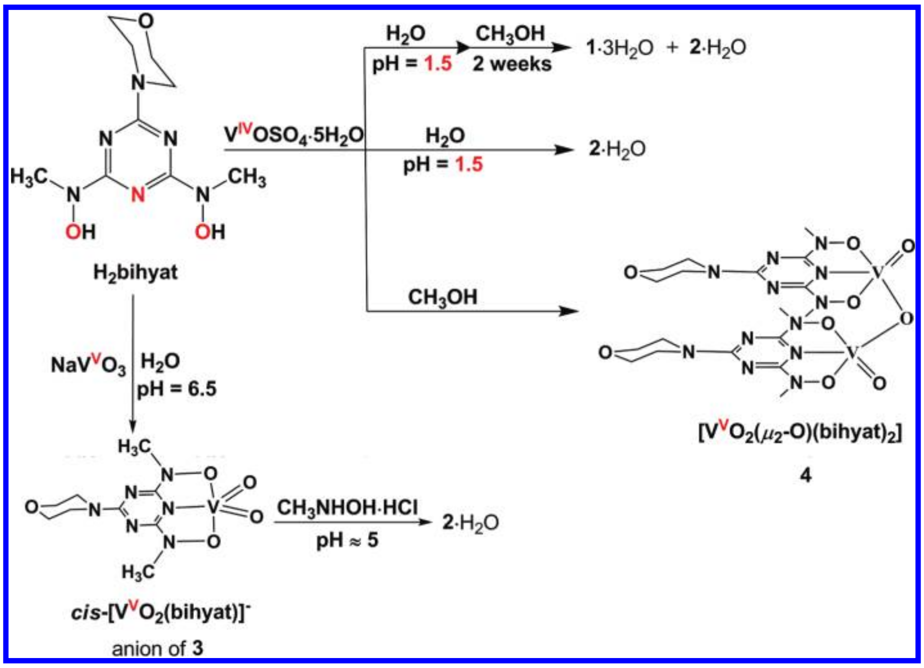
(16) (a) *CrystAlisCCD*, version 1.171.32.5; *CrysAlis RED*, version 1.171.32.59; Oxford Diffraction Ltd: Oxfordshire , U. K., 2007.(b) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

Scheme 4. Synthesis of the Compounds $\mathbf{1}\cdot 3H_2O$, $\mathbf{2}\cdot H_2O$, **3**, and **4** (from ref 13)



dissolving crystalline material in anhydrous CD_2Cl_2, just prior to the NMR experiment.

Physical Measurements. IR spectra of the various compounds dispersed in KBr pellets were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Electronic absorption spectra were measured as solutions in septum-sealed quartz cuvettes on a Jasco V570/UV/vis/NIR spectrophotometer. Solid-state UV−vis spectra were obtained at room temperature on a Shimadzu UV-3101PC double-beam, double monochromator spectrophotometer in the wavelength range of 200−900 nm. $BaSO_4$ powder was used as a reference (100% reflectance) and base material on which the powder sample was coated. Reflectance data were converted to absorbance data as described elsewhere.[17]

Electrospray Mass Spectroscopy (ESI-MS). Electrospray mass spectra were obtained on a Micromass Platform II quadrupole mass spectrometer. Samples were dissolved in H_2O or methyl alcohol and injected into the ESI source at a flow rate of 5 μL/min. The source temperature was adjusted to 60 °C, while the cone voltage was set to 60 V.

Results and Discussion

Syntheses. The synthesis of the vanadium(V) compounds $\mathbf{1}\cdot 3H_2O$, $\mathbf{2}\cdot H_2O$, $C(NH_2)_3[V^VO_2(bihyat)]$ (**3**),[13] and $[V^V{}_2O_3(bihyat)_2]$ (**4**)[13] is shown in Scheme 4. The isolation of the compounds $\mathbf{1}\cdot 3H_2O$−**4** reveals the very rich chemistry of H_2bihyat with vanadium(V).

Compound $\mathbf{2}\cdot H_2O$ was synthesized (method A) by treating an aqueous solution (40 mM) of $V^{IV}OSO_4\cdot 5H_2O$ with H_2bihyat in a molar ratio of 1:1 in 13% yield. The ligand CH_3NHO^- in $[V^VO(bihyat)(CH_3NHO)]\cdot H_2O$ ($\mathbf{2}\cdot H_2O$) results presumably from the cleavage of one carbon−nitrogen bond [C−N(OH)CH_3] of the ligand H_2bihyat (see ESI-MS Spectroscopy and ^1H and ^{51}V NMR studies in ref 13), and this simply means that 1 equiv of H_2bihyat is consumed for this purpose. Taking also into account the fact that Hhyta and Hhyto are also formed from the decomposition of H_2bihyat in the presence of $V^{IV}OSO_4\cdot 5H_2O$ in water (see ESI-MS Spectroscopy), one expects that, when reacting $V^{IV}OSO_4\cdot 5H_2O$ with H_2bihyat in a molar ratio ≥ 1:2, the yield of the reaction should increase, and this was indeed the case with 52% yield in a 1:2 ratio (see Experimental Section) and 56% in a 1:3 molar ratio. Compound $\mathbf{2}\cdot H_2O$ was also prepared (method B) by sequential addition of equivalent quantities of H_2bihyat and methyl hydroxylamine hydrochloride to a solution of NaV^VO_3 in water (eqs 1 and 2) following the literature for the preparation of similar compounds.[10a]

$$NaV^VO_3 + H_2bihyat \rightarrow \underset{\text{anion of } \mathbf{3}}{cis\text{-}[V^VO_2(bihyat)]^-} + Na^+ + H_2O \qquad (1)$$

$$cis\text{-}[V^VO_2(bihyat)]^- + CH_3NHOH\cdot HCl \rightarrow \underset{\mathbf{2}}{[V^VO(bihyat)(CH_3NHO)]} + H_2O + Cl^- \qquad (2)$$

When the reaction of $V^{IV}OSO_4\cdot 5H_2O$ [C = 20 mM] with the ligand H_2bihyat was conducted first in water (6 h) followed by the addition of methyl alcohol, the asymmetric divanadium(V) compound $\mathbf{1}\cdot 3H_2O$ and the methylhydroxylamido derivative $\mathbf{2}\cdot H_2O$ (Scheme 4) were formed after two weeks.

If the solvent of the reaction of $V^{IV}OSO_4\cdot 5H_2O$ with H_2bihyat was methyl alcohol, the symmetric divanadium(V) compound, $[V_2{}^VO_2(\mu_2\text{-}O)(bihyat)_2]$ (**4**), was isolated[13] (Scheme 4). Thus, the solvent is crucial for the formation of either the asymmetric $\mathbf{1}\cdot 3H_2O$ or the symmetric (**4**) divanadium(V) compounds. The case is under further investigation.

ESI-MS Spectroscopy. In an effort to further investigate the effect of vanadium, in various oxidation states (III, IV, and V), on the decomposition of the ligand

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[17] McCarthy, T. J.; Ngeyi, S. P.; Liao, J. H.; Degroot, D. C.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 331.

Table 2. ESI-MS Data from the Interaction of the Ligand H_2bihyat with the Vanadium(III,IV) Species and of the Compound $[C(NH_2)_3][V^VO_2(bihyat)]$ at Various pH's

vanadium compound	solvent	pH	*m*/*z* of the positive mode fragmentation ions (relative intensity, %)	assignment
$[C(NH_2)_3][V^VO_2(bihyat)]^a$	water	6.5^b	337.47 (100%) (negative mode)	*cis*-$[V^VO_2(bihyat)]^-$
$[C(NH_2)_3][V^VO_2(bihyat)]^a$	water	1.5	228.23 (100%), 368.35 (30%), 257.32 (18%)	H_2hyto^+, $[V^VO)(Hbihyat)(CH_3NHO]^+$, $H_3bihyat^+$
$V^{IV}OSO_4\cdot 5H_2O^c$	water	1.5	241.25 (100%), 257.32 (60%), 228.23 (30%), 368.35 (10%)	H_2hyta^+, $H_3bihyat^+$, H_2hyto^+, $[V^VO(Hbihyat)(CH_3NHO)]^+$
$V^{IV}OSO_4\cdot 5H_2O^c$	methyl alcohol		241.25 (100%)	H_2hyta^+
$V^{III}Cl_3{}^c$	water	1.0	241.25 (100%), 257.32 (30%)	H_2hyta^+, $H_3bihyat^+$

[a] From ref 13. [b] The ESI-mass spectrum of $[C(NH_2)_3][V^VO_2(bihyat)]$ was also recorded at pH values 5.0, 4.0, and 3.0, and only the molecular ion *cis*-$[V^VO_2(bihyat)]^-$ was detected. [c] The ESI-MS measurements were performed 6 h after the preparation of the samples.

H_2bihyat, ESI-MS measurements were performed (Table 2). The ESI-MS spectrum (+ve) of an aqueous solution (pH = 1.5) containing equivalent quantities of $V^{IV}OSO_4\cdot 5H_2O$ and H_2bihyat ($C \approx 20$ mM) revealed the presence of four characteristic molecular ions at 241.25 (100%), 257.32 (60%), 228.33 (30%), and 368.35 (10%), which were assigned to the singly protonated forms of the ligands Hhyta, H_2bihyat, Hhyto, and compound **2**, respectively. The ligands H_2bihyat, Hhyta, and Hhyto, then chelate to vanadium(V) to form compound **1** under the specific conditions described in the Experimental Section. The ESI-MS spectrum (+ve) of a methyl alcohol solution containing equivalent quantities of $V^{IV}OSO_4\cdot 5H_2O$ and H_2bihyat ($C \approx 20$ mM) revealed the presence of only one molecular ion at 241.25 (100%), which was assigned to the singly protonated form of Hhyta, indicating the limited fragmentation of H_2bihyat under the same experimental conditions using less polar solvents. The ESI-MS spectrum (+ve) of an aqueous solution (pH ≈ 1) containing equivalent quantities of $V^{III}Cl_3$ and H_2bihyat ($C \approx 20$ mM) revealed the presence of two molecular ions at 241.25 (100%) and 257.32 (30%), which were assigned to the singly protonated forms of the ligands Hhyta and H_2bihyat. Interestingly, in the latter case, the fragmentation process is not as extensive as in the case where vanadium(IV) was used. As expected (from ^{51}V and ^{1}H NMR and potentiometry),[13] the ESI-MS spectrum (−ve) of compound $[C(NH_2)_3][V^VO_2(bihyat)]$ **3**[13] ($C \cong 20$ mM) in water and at pH values 6.5, 5.0, 4.0, and 3 revealed only the presence of the molecular ion at 337.47 (100%), which corresponds to the species *cis*-$[V^VO_2(bihyat)]^-$. At lower pH values, such as 1.5, three species were detected in the ESI-MS spectrum (+ve) of **3**, at 228.23 (100%), 368.35 (30%), and 257.32 (18%), and were assigned to the protonated forms of Hhyto, **2**, and H_2bihyat, respectively.

The above-mentioned solution studies revealed that the polar solvents (H_2O, CH_3OH) promote the decomposition of the ligand H_2bihyat in the presence of vanadium in oxidation states III, IV, and V. More specifically, the extent of the ligand's fragmentation at low pH values (1−1.5) follows the series $V^{IV} > V^V > V^{III}$. It is also clear that vanadium(IV) triggers the partial fragmentation of H_2bihyat to Hhyta and Hhyto, and then, the coexisting three ligands in solution chelate to the vanadium(V) to form the asymmetric divanadium(V) compound $[V_2{}^VO_2(\mu_2\text{-}O)(bihyat)(hyta)(hyto)]$. Further solution studies using a micro-TOF high-resolution CSI apparatus[18] ($T \approx -100$ °C) along with theoretical calculations could potentially shed light on the seemingly complicated formation mechanism[19] of $\mathbf{1}\cdot 3H_2O$ and $\mathbf{2}\cdot H_2O$.

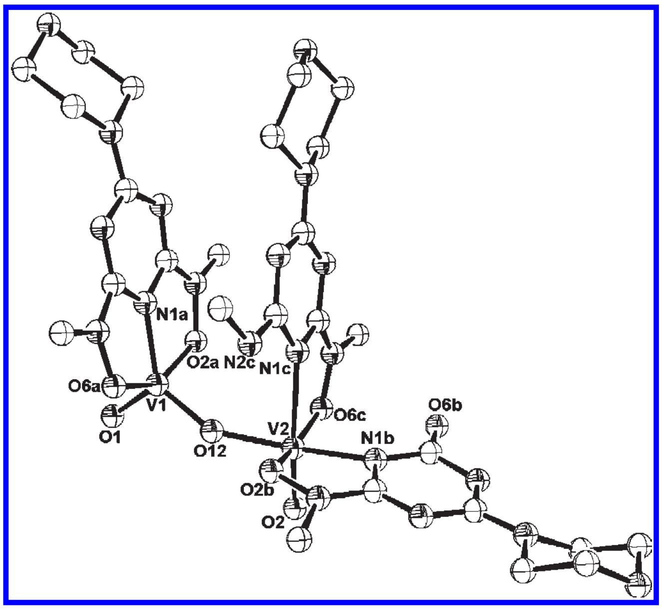

Figure 1. ORTEP representation of the compound $\mathbf{1}\cdot 3H_2O$ at 50% probability ellipsoids, giving atomic numbering.

Crystal Structures. The molecular structure of $\mathbf{1}\cdot 3H_2O$ is shown in Figure 1. A selection of interatomic distances and bond angles relevant to the vanadium coordination sphere in $\mathbf{1}\cdot 3H_2O$ is listed in Table 3. One five-coordinate atom, V(1), and one six-coordinate, V(2), vanadium(V) atom are bridged by an oxygen atom O(12) to form the unsymmetrical compound $\mathbf{1}\cdot 3H_2O$. In $\mathbf{1}\cdot 3H_2O$, the bridge is asymmetric with d[V(1)−O(12)] = 1.711(3) Å and d[V(2)−O(12)] = 1.927(3) Å, with the longer bond directed toward the six-coordinate vanadium atom. The vanadium atom V(1) has a distorted square pyramidal geometry ($\tau = 0.308$),[20] and it is bonded to a tridentate bihyat^{2-} ligand at the triazine nitrogen atom and the two deprotonated hydroxylamido oxygen atoms, a μ_2- bridging oxido group, and a terminal oxido ligand. The uniquely short V(1)−N(1a) bond length of 1.964(4) Å, which is even shorter than the V^V-N_{amide}

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[19] (a) Long, D.-L.; Kogerler, P.; Cronin, L. *Dalton Trans.* **2008**, 214–221. (b) Miras, H. N.; Stone, D. J.; McInnes, E. J. L.; Raptis, R. G.; Baran, P.; Chilas, G. I.; Sigalas, M. P.; Kabanos, T. A.; Cronin, L. *Chem. Commun.* **2008**, 4703–4705.

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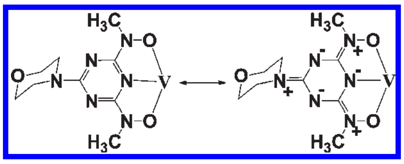
Table 3. Interatomic Distances (Å) and Angles (deg) Relevant to the Vanadium(V) Coordination Sphere for the Compounds **1**·3H_2O and **2**·H_2O

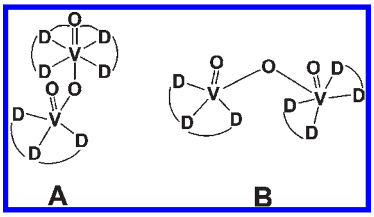
parameter	**1**·3H_2O	parameter	**2**·H_2O
V(1)−O(1)	1.601(3)	V(1)−O(1)	1.596(3)
V(1)−O(2a)	1.972(3)	V(1)−O(2)	1.977(3)
V(1)−O(6a)	1.942(3)	V(1)−O(6)	1.972(2)
V(1)−N(1a)	1.964(4)	V(1)−N(1)	1.966(3)
V(1)−O(12)	1.711(3)	V(1)−O(1a)	1.886(3)
V(2)−N(1b)	2.093(4)	V(1)−N(1a)	2.029(3)
V(2)−N(1c)	2.280(4)		
V(2)−O(2)	1.606(3)		
V(2)−O(12)	1.927(3)		
V(2)−O(2b)	1.971(3)		
V(2)−O(6c)	1.871(3)		
O(1)−V(1)−O(12)	109.94(12)	O(1)−V(1)−O(1a)	109.35(16)
O(1)−V(1)−O(2a)	97.81(15)	O(1)−V(1)−O(2)	102.17(11)
O(1)−V(1)−O(6a)	100.04(14)	O(1a)−V(1)−O(2)	78.34(10)
O(12)−V(1)−O(2a)	98.52(13)	O(1a)−V(1)−O(6)	112.70(10)
O(12)−V(1)−O(6a)	99.05(13)	O(1)−V(1)−O(6)	107.62(12)
O(6a)−V(1)−O(2a)	149.11(15)	O(6)−V(1)−O(2)	141.34(10)
O(1)−V(1)−N(1a)	120.00(15)	O(1A)−V(1)−N(1a)	41.11(11)
O(12)−V(1)−N(1a)	130.63(15)	O(1)−V(1)−N(1a)	97.44(13)
O(6a)−V(1)−N(1a)	74.73(15)	O(2)−V(1)−N(1a)	119.39(11)
N(1a)−V(1)−O(2a)	74.54(15)	O(1)−V(1)−N(1)	104.48(12)
V(1)−O(12)−V(2)	151.50(17)	O(1a)−V(1)−N(1)	140.14(12)
		O(6)−V(1)−N(1a)	80.78(11)
O(2)−V(2)−O(6c)	92.65(15)	N(1)−V(1)−O(2)	75.27(11)
O(2)−V(2)−O(12)	99.08(14)	N(1)−V(1)−O(6)	73.86(11)
O(6C)−V(2)−O(12)	100.71(13)	N(1)−V(1)−N(1a)	150.43(12)
O(2)−V(2)−O(2b)	103.33(14)		
O(6c)−V(2)−O(2b)	162.63(14)		
O(12)−V(2)−O(2b)	83.66(12)		
O(2)−V(2)−N(1b)	94.70(15)		
O(6c)−V(2)−N(1b)	95.25(14)		
O(12)−V(2)−N(1b)	158.33(14)		
O(2b)−V(2)−N(1b)	76.91(13)		
O(2)−V(2)−N(1c)	166.18(15)		
O(6c)−V(2)−N(1c)	73.61(14)		
O(12)−V(2)−N(1c)	82.42(13)		
O(2b)−V(2)−N(1c)	90.50(13)		
N(1b)−V(2)−N(1c)	88.18(14)		

bond length[21] of ≈2.0 Å, was attributed to the high electron density of the cyclic triazine nitrogen atoms, which results from the resonative contribution of electrons of the exocyclic nitrogen atoms (Scheme 5). The vanadium atom V(2) has a highly distorted octahedral geometry, and it is bonded to a terminal oxygen atom, to the oxygen atom bridging the two vanadium atoms and the two cyclic triazine nitrogen atoms, and to the two deprotonated hydroxylamido oxygen atoms of the ligands hyta$^-$ and hyto$^-$. The distances d[V(2)−N(1b)] = 2.093(4) and d[V(2)−N(1c)] = 2.280(4) Å have been substantially elongated in comparison with the d[V(1)−N(1a)] = 1.964(4) Å due to the strong trans influence of the μ_2-bridging and terminal oxido groups, respectively. The planes of the ligands bihyat^{2-} and hyta$^-$ are almost parallel (Figure 1), as judged by the near zero value of the dihedral angle between them (6.8°). The unsymmetrical μ-oxido divanadium(V) compounds thus far reported in the literature[14] contain a tetradentate and a tridentate ligands attached to the vanadium(V) atoms (Scheme 6A), and the tetradentate ligand forces the μ_2-oxido group into a trans position [$\angle$(O=V−O$_b$) ≈ 170−175°] in the six-coordinate vanadium atom with a long V−O$_b$ distance of ≈2.16 Å. Compound **1**·3H_2O contains two bidentate and a tridentate ligand bound to the vanadium atoms (Scheme 6B). The ligation of the two bidentate ligands to the six-coordinate vanadium atom allows a cis configuration for the terminal and μ_2-oxido groups [$\angle$(O=V−O) = 99.08(14)°], and thus, the d(V−O$_b$) of 1.927(3) Å is shorter in comparison with that reported in the unsymmetrical μ_2-O^{2-} divanadium(V) compounds[14] (Table 4). The d[V(1)···V(2)] in **1**·3H_2O is 3.526(11) and lies in the middle in comparison with the other asymmetrical divanadium(V) compounds[14] (Table 4). From Table 4, it is clear that the V(1)···V(2) distance is mainly dependent on the $\angle$[V(1)−O$_b$−V(2)], and as this angle is reduced, the d[V(1)···V(2)] is also reduced and vice versa. The conformation of the $V^V{}_2O_3{}^{4+}$ core is *syn*-angular with a torsion angle of −1.6° (Table 4) between V(1)=O(1) and V(2)=O(2).

Scheme 5



Scheme 6



An ORTEP structural plot for compound **2**·H_2O is presented in Figure 2. The coordination environment of the vanadium atom in **2**·H_2O approximates to a highly distorted pentagonal pyramid with the oxido ligand occupying the apical position and the donor atoms of the tridentate ligand bihyat^{2-} and of the bidentate ligand CH_3NHO^- the basal plane. The three basal atoms of bihyat^{2-} deviate slightly from the least-squares basal plane [N(1), 0.029(16); O(2), 0.055(15); and O(6), 0.083(16) Å], while the two donor atoms of the N-methyl-hydroxylamido group deviate substantially from the least-squares basal plane [N(1a), 0.195(19) and O(1a), 0.196(19) Å]. The vanadium atom is 0.49 Å above the mean basal plane toward the oxido group. The deprotonated methylhydroxylamido ligand, CH_3NHO^-, is bound to the vanadium atom in a side on (N,O) fashion.[10,22]

All of the elucidated structures of unmodified hydroxylamine and of N-alkyl-substituted hydroxylamine with [V^V=O]$^{3+}$ are deprotonated.[10,13,22] The mean N−O bond length for these hydroxylamido vanadium(V) derivatives is ~1.39 Å. The V−O and V−N bonds are similar in length, with mean values of approximately 1.90 and

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Table 4. Comparison of a Few Structural Features [Angles (deg) and Bond Distances (Å)] of $\mathbf{1}\cdot 3H_2O$ with the Reported Unsymmetrical μ_2-O^{2-} Divanadium Compounds[14]

parameter	compound				
	$\mathbf{1}\cdot 3H_2O$	$\mathbf{2}'^{d}$	$\mathbf{3}'^{d}$	$\mathbf{4}'^{d}$	$\mathbf{5}'^{d}$
$\angle$[V(1)−O−V(2)][a]	151.50(17)	158.76(9)	117.92(8)	166.20(9)	157.79(16)
torsion angle[b]	−1.6	−38.87	−178.35	−50.59	33.20
dihedral angle[c]	18.8	75.63	10.44	80.81	81.79
d[V(1)···V(2)]	3.525(11)	3.7633(5)	3.3084(6)	3.7921(7)	3.7395(13)
$\angle$[O=V(2)−O$_b$]	99.08(14)°	170.41(7)	174.67(8)	171.89(8)	173.28(14)
d[V(2)−O$_b$]	1.927(3) Å	2.1772(15)	2.1658(16)	2.1461(16)	2.140(3)

[a] V(1) and V(2) correspond to the five-coordinate and six-coordinate vanadium atoms, respectively. [b] Torsion angle between V(1)=O$_t$ and V(2)=O$_t$. [c] Dihedral angle formed by O$_t$, V(1), O$_b$ and O$_b$, V(2), and O$_t$ planes. [d] Compounds **2′**, **3′**, **4′**, and **5′** correspond to compounds **2**, **3**, **4**, and **5** reported in ref 14.

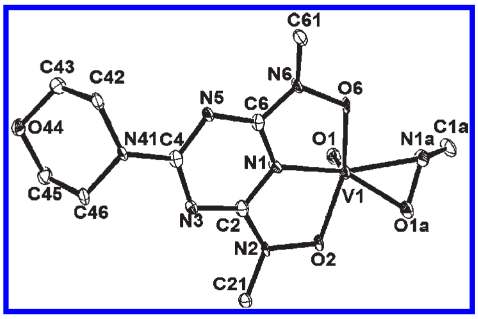
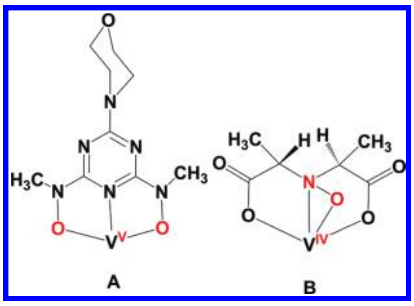


Figure 2. ORTEP representation of the compound $\mathbf{2}\cdot H_2O$ at 50% probability ellipsoids, giving atomic numbering.

2.02 Å, respectively. The bond lengths of ~1.90, ~2.03, and ~1.38 Å for the bonds V−O, V−N, and N−O, respectively, for the N-methyl-hydroxylamido ligand CH_3NHO^- in $\mathbf{2}\cdot H_2O$ are almost identical with the above-mentioned values for V^V=O−hydroxylamido compounds. The chelating bis-(hydroxylamido) ligand bihyat^{2-} in compounds $\mathbf{1}\cdot 3H_2O$ and $\mathbf{2}\cdot H_2O$ has average V−O and N−O bond lengths of ~1.97 and ~1.40 Å, respectively. The elongated V−O bond is presumably due to the fact that the two hydroxylamido oxygens are in a trans position in both compounds.

H_2bihyat Binding to Vanadium in Comparison with the Biological Ligand H_3hidpa. The ligand bihyat^{2-} binds to vanadium via an [O, N, O′] tridentate binding mode (Scheme 7A), while the ligand hidpa^{3-}, found in amavadine, binds to the vanadium via an [O, N, O′, O″] tetradentate binding mode (Scheme 7B). When the hydroxyl group, of unmodified hydroxylamine, its N-alkyl functionalized variants, and the chelating hydroxylamino ligand H_3hidpa, is deprotonated, it coordinates to the vanadium atom in a side-on fashion (Scheme 7B). The chelating bis-(hydroxylamido) ligand bihyat^{2-} is an exception to this general trend, since it binds to the vanadium atom with the deprotonated hydroxyl oxygen atoms only, with the nitrogen atoms not participating in metal coordination. The ligating behavior of bihyat^{2-} was attributed to a deficient electronic cloud on the exocyclic nitrogens of it, owing to the large contribution of the resonative structure "B" in $\mathbf{1}\cdot 3H_2O$−**4** (Scheme 5). The resonative structure "B" was proposed on the basis of crystallographic data for compounds $\mathbf{1}\cdot 3H_2O$, $\mathbf{2}\cdot H_2O$, **3**,[13] and **4**[13] and of the literature data.[12] In addition, the ligand bihyat^{2-} forms only oxidovanadium compounds, with the vanadium in its highest oxidation state, that is, V, while the biological ligand hidpa^{3-} gives the nonoxido vanadium(IV) compound $[V^{IV}(hidpa)_2]^{2-}$.

Scheme 7



NMR Spectroscopy. The ^{51}V NMR spectrum of $\mathbf{1}\cdot 3H_2O$, in anhydrous CD_2Cl_2, was recorded at room temperature and revealed the presence of two signals resonating at −199 and −508 ppm with a 1:1 relative ratio of peak integrals and $\Delta\nu$ values of 1.79 kHz and 3.42 kHz, respectively (Figure 3). The two peaks have been assigned to the five- and the six-coordinate vanadium(V) atoms of the complex, supporting the claim that the asymmetric structure of $\mathbf{1}\cdot 3H_2O$ is retained in solution. On the basis of the donor atoms' electronegativity (N and O) and applying Rehder's referencing scale,[23] one could predict chemical shift values for such vanadium(V) compounds in the upfield region between −400 and −600 ppm. According to the same referencing scale,[23] the five-coordinate vanadium(V) is expected to give chemical shift values in a weaker field than six-coordinate vanadium(V).[23] In addition, the five-coordinate vanadium(V) should have a smaller line width of the peak than that of the six-coordinate vanadium(V).[24] The peak at −508 ppm falls in the expected region of −400 to −600 ppm, and it was assigned to the six-coordinate vanadium atom V(2). This assignment was also supported by the line width of the peak (3.42 kHz), which is almost double of the peak's line width of the five-coordinate vanadium atom in compound $Ph_4P[V^VO_2(bihyat)]\cdot 1.5H_2O$[13] (line width 1.98 kHz). On the other hand, the peak at −199 ppm has a line width of 1.79 kHz, which is similar to the line width of the five- coordinate vanadium atom in compound $Ph_4P[V^VO_2(bihyat)]\cdot 1.5H_2O$[13] and it was assigned to the five-coordinate "$[V(1)O_2(bihyat)]$" moiety of $\mathbf{1}\cdot 3H_2O$. The resonance of the V(1) nucleus in a field much lower than the expected from Rehder's scale[23] was attributed to the low-energy

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(23) Rehder, D.; Weidemann, C.; Duch, A.; Priebsch, W. *Inorg. Chem.* **1988**, *27*, 584–587.
(24) Crans, D. C.; Shin, P. *J. Am. Chem. Soc.* **1994**, *116*, 1305–1318.

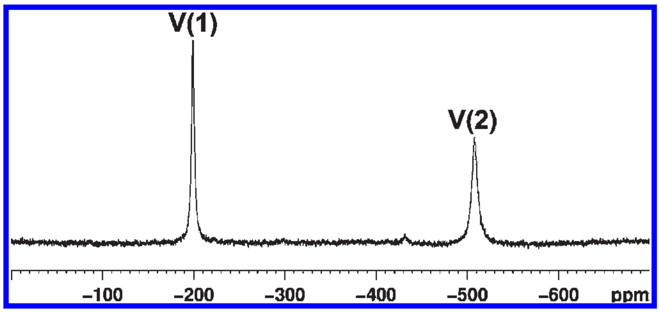

Figure 3. ^{51}V NMR spectrum of compound $\mathbf{1}\cdot 3H_2O$ in anhydrous CD_2Cl_2 recorded at 296 K.

Table 5. ^{1}H, ^{13}C, and ^{51}V NMR Chemical Shifts (δ, ppm) for the Ligand H_2bihyat and the Compounds $\mathbf{1}\cdot 3H_2O$, $\mathbf{2}\cdot H_2O$, and $(Ph_4P)[V^VO_2(bihyat)\cdot 1.5H_2O$[a]

	H_2bihyat[a]	$\mathbf{1}\cdot 3H_2O$[b]	$\mathbf{2}\cdot H_2O$[c]	$Ph_4P[V^VO_2$-(bihyat)]$\cdot$ 1.5H_2O
C_1, H_1	43.84, 3.75	(43.67−44.38), (3.6−3.8)	43.97, 3.89 43.97, 3.60	44.27, 3.78
C_2, H_2	66.46, 3.68	(66.01−66.6), (3.6−3.8)	66.57, 3.71 66.57, 3.60	66.82, 3.66
C_3	163.22	nd[d]	163	164.83
C_4	164.97	158.81	157.8	159.70
$C_{4'}$		nd[d]		
$C_{4''}$		163.04		
C_5	164.97	159.02		159.70
$C_{5'}$		nd[d]		
$C_{5''}$		156.38		
C_6, H_6	36.15, 3.32	35.32, 3.29	35.7, 3.41	35.28, 3.28
$C_{6'}$, $H_{6'}$		39.66, 3.87		
$C_{6''}$, $H_{6''}$		27.18, 2.81		
C_7, H_7		35.43, 3.32	7_a: 45.2, 3.5 7_b: 40.02, 3.11	
$C_{7''}$, $H_{7''}$		37.19, 3.49		
H_8		7.60	8_a: 7.86 8_b: 8.17	
^{51}V		−199, −508	−667, −688	−502

[a] NMR data were acquired at 296 K. [b] NMR data were acquired at 278 K. [c] NMR data were acquired at 245 K. [d] nd: not determined.

ligand-to-metal charge transfer (LMCT) transition (605 nm with $\varepsilon_M = 5\,050\ M^{-1}\ cm^{-1}$), which $\mathbf{1}\cdot 3H_2O$ exhibits in solution. According to Pecoraro et al.,[25a] the vanadium nucleus becomes more deshielded as the LMCT energy is decreased,[25] and this is in line with the observed chemical shift for $\mathbf{1}\cdot 3H_2O$. Similar deshielding of the vanadium(V) nucleus was also observed in the oxidized amavadine.[8b]

To further investigate the solution structure of $\mathbf{1}\cdot 3H_2O$, 1D and 2D NMR experiments were performed. ^{1}H and ^{13}C NMR chemical shifts of $\mathbf{1}\cdot 3H_2O$, of the ligand H_2bihyat, and of the compound $(Ph_4P)[V^VO_2(bihyat)]\cdot 1.5H_2O$[13] are shown in Table 5. All data were acquired at 296 K from freshly prepared solutions of crystalline material in anhydrous CD_2Cl_2, while the time-consuming 2D experiments were recorded at 278 K in order to ensure the stability of $\mathbf{1}\cdot 3H_2O$ during measurements. The ^{1}H NMR spectra of $\mathbf{1}\cdot 3H_2O$, of the ligand H_2bihyat, and of $Ph_4P[V^VO_2(bihyat)]\cdot 1.5H_2O$ at 296 K are shown in Figure 4. The methyleno protons $H_{1,1',1''}$ and $H_{2,2',2''}$ of the three morpholine rings of the ligands bihyat^{2-}, hyta^{-}, and hyto^{-} resonate in the region of 3.6−3.9 ppm. Compound $\mathbf{1}\cdot 3H_2O$ contains five methyl groups attached to nitrogen atoms, and thus, four singlets and a doublet (due to coupling of the methyl protons to the neighboring N−H proton) were expected. In the ^{1}H NMR spectrum of $\mathbf{1}\cdot 3H_2O$, three singlets at 3.49, 3.32, and 3.29 ppm (in a 1:1:1 ratio) and a doublet at 2.81 ppm can be distinguished. The doublet was assigned to C(6″) methyl protons attached to the secondary amine group −N−H (the 2D DQF-COSY spectrum of $\mathbf{1}\cdot 3H_2O$ confirmed this correlation), and the two singlets at 3.32 and 3.29 ppm were assigned to the methyl protons of C(6) and C(7) carbons of bihyat^{2-} on the basis of the fact that the corresponding protons of the bihyat^{2-} in the monomer $Ph_4P[V^VO_2(bihyat)]\cdot 1.5H_2O$[13] and of H_2bihyat resonate at 3.28 and 3.32 ppm, respectively. The chemical shift difference of 0.03 ppm between the C(6) and C(7) methyl protons was attributed to the nonequivalent environment of the two methyl groups induced from the asymmetry of the "$[V^VO_2(hyto)(hyta)]$" part of the molecule.

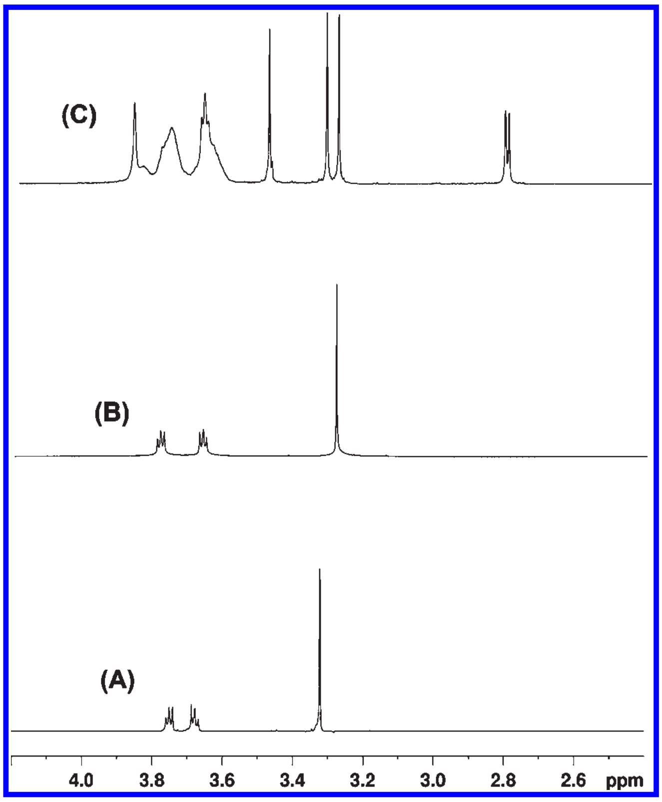

Figure 4. ^{1}H NMR spectra of the ligand H_2bihyat (A), $Ph_4P[V^VO_2$-(bihyat)]$\cdot 1.5H_2O$ (B), and $\mathbf{1}\cdot 3H_2O$ (C), recorded at 296 K.

To assign the peak at 3.49 ppm and to discover one missing signal due to the methyl protons of the ligand hyto^{-}, an ^{1}H−^{13}C HSQC experiment was performed. Figure 5 shows the 2D ^{1}H−^{13}C HSQC map of $\mathbf{1}\cdot 3H_2O$. The morpholine carbon atoms C(1,1′,1″) and C(2,2′,2″) of the ligands bihyat^{2-}, hyta^{-}, and hyto^{-} resonate at ~44 and ~66 ppm, respectively (Figure 5), while the methyl carbons resonate in the region 30−40 ppm. Thus, the cross peak of the protons at 3.87 ppm and of the carbon at 39.6 ppm should be assigned to the methyl group of hyto^{-}

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(25) (a) Cornman, C. R.; Colpas, G. J.; Hoeschele, J. D.; Kampf, J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1992**, *114*, 9925–9933. (b) Drouza, C.; Keramidas, A. D. *Inorg. Chem.* **2008**, *47*, 7211–7224. (c) Rehder, D; Polenova, T.; Buhl, M. *Annu. Rep. NMR Spectrosc.* **2007**, *62*, 49–114.

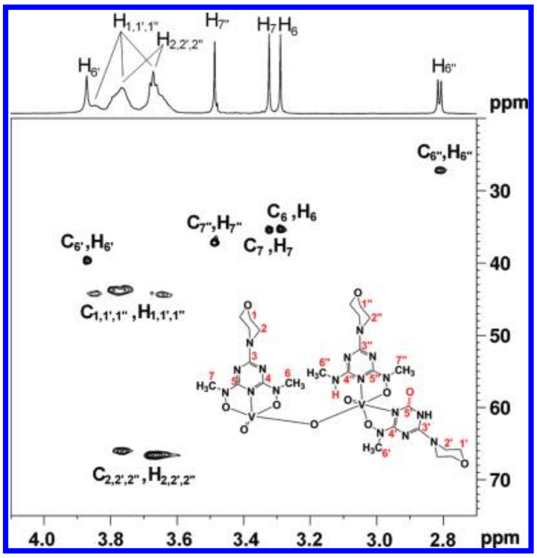

Figure 5. Selected region of the $^1H-^{13}C$ HSQC spectrum of compound **1**$\cdot$3H_2O at 278 K. The assignment of the protons directly attached to carbons is shown.

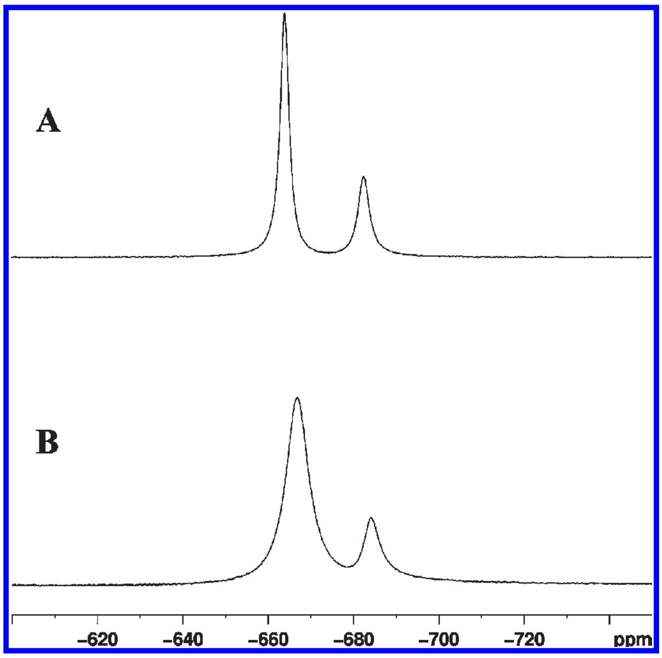

Figure 6. ^{51}V NMR spectrum of compound **2**$\cdot H_2O$ in CD_2Cl_2 recorded at 296 (A) and 245 K (B).

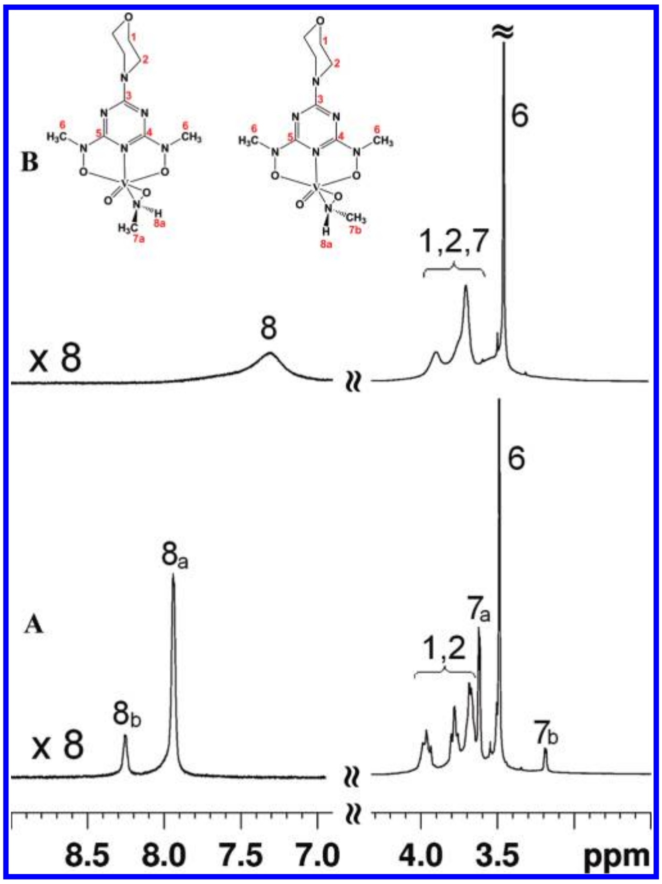

Figure 7. ^1H NMR spectra of compound **2**$\cdot H_2O$ recorded at 245 (A) and at 296 K (B). The assignment of the protons of the two isomers is indicated.

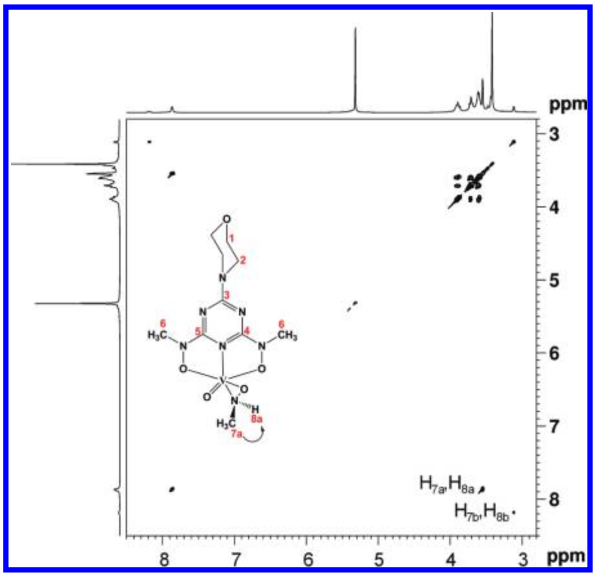

Figure 8. Selected region of the $^1H-^1H$ DQF COSY of compound **2**$\cdot H_2O$ at 245 K, showing the correlation between the C(7) and NH(8) resonances.

C′(6) and the signal at 3.49 ppm to the respective methyl protons of C(7″).

The ^{51}V NMR spectrum of compound **2**$\cdot H_2O$ in CD_2Cl_2 at room temperature (296 K) revealed the presence of two signals resonating at −682 and −664 ppm with a relative ratio of ~0.4:1, which strongly suggested the presence of a mixture of two isomers (Figure 6A).[10a,c,26] Thus, variable-temperature ^{51}V and ^1H NMR spectra acquisition was utilized for the structure elucidation of the two isomers. At 245 K, the two ^{51}V NMR signals of **2**$\cdot H_2O$ appeared at −684 and −667 ppm with a relative ratio of 0.3:1 (Figure 6B). In Figure 7, the ^1H NMR spectra of **2**$\cdot H_2O$ at 296 and 245 K are demonstrated. At 296 K, the ^1H NMR spectrum gave broad peaks which at 245 K became sharp, indicating that the two isomers are in dynamic equilibrium. The spectrum at 245 K gave signals from both isomers. Some characteristic features are the two CH(7) (3.11 and 3.55 ppm) and two NH(8)

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(26) Angus-Dunne, S. J.; Paul, P. C.; Tracey, A. S. *Can. J. Chem.* **1997**, *75*, 1002–1010.

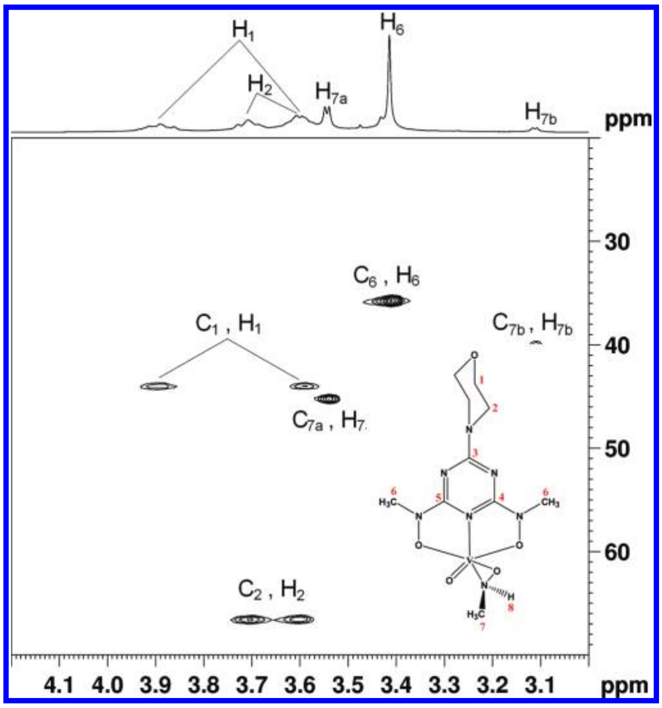

Figure 9. Selected region of the $^1H-^{13}C$ HSQC spectrum of compound **2**·H_2O at 245 K. The assignment of the protons directly attached to carbon atoms is shown.

proton (8.17 and 7.86 ppm) signals for isomers **b** and **a**, respectively (Table 5). The $^1H-^1H$ DQF-COSY experiment was performed at 245 K and revealed the correlation between the C(7) and NH(8) proton resonances at 3.11 and 8.17 ppm and 3.55 and 7.86 ppm, respectively (Figure 8). The assignments were based on the expected deshielding from the V=O bond of the groups in its neighborhood, the CH(7) in isomer **a** and the NH(8) in isomer **b**. The suggested assignment was further confirmed from the 2D $^1H-^{13}C$ HSQC experiment (Figure 9), where the following cross peaks were observed: morpholine group, (3.6, 43.97), (3.89, 43.97), (3.60, 66.5), (3.71, 66.57); N−C(6) (3.41, 35.7), C(7a) (3.11, 40.02), C(7b) (3.55, 45.2). The crystallographically characterized structure of compound **2**·H_2O is similar to the isomer **a** which is the most stable isomer in solution.

Conclusions

In conclusion, an unexpected synthesis of an unsymmetrical divanadium(V) compound $[V^V{}_2O_2(\mu_2\text{-}O)(\text{bihyat})(\text{hyta})(\text{hyto})]\cdot 3H_2O$ was achieved through an unusual reductive cleavage of an N−O and cleavage-hydrolysis of a C−N bond of the N,N-disubstituted bis-(hydroxylamino) ligand, H_2bihyat. The chelating hydroxylamido ligand, bihyat^{2-}, forms only compounds with vanadium(V), while the chelating hydroxylamido ligand, hidpa^{3-} in amavadine, stabilizes vanadium in oxidation state IV. The ligand hidpa^{3-} in amavadine, the deprotonated hydroxylamine NH_2O^-, and N-alkyl substituted hydroxylamido derivatives bind to the vanadium atom in a side-on (N,O) fashion. This is not the case with the chelating hydroxylamido-based ligands bihyat^{2-}, hyta$^-$, and hyto$^-$, which bind to the vanadium via the deprotonated hydroxyl oxygen atom only. ESI-MS studies on the system vanadium(III/IV/V)−H_2bihyat revealed that the fragmentation of the ligand H_2bihyat is a complicated process depending on the solvent, oxidation state of vanadium, and pH value. The polarity of the solvent favors the cleavage of H_2bihyat, while the oxidation state IV of vanadium triggers this transformation. More specifically, we showed that the fragmentation of H_2bihyat is more extensive according to the series $V^{IV} > V^V > V^{III}$.

The solution ^{51}V NMR spectrum of **1**·$3H_2O$ gave two signals at −199 and −508 ppm with a 1:1 relative ratio of peak integrals and were assigned to the five- and the six-coordinate vanadium(V) atoms, respectively. The signal at −199 ppm is significantly downfield of the "normal" shift range for a vanadium atom with nitrogen and oxygen donor atoms. The dominant factor in the dishielding of this vanadium nucleus is the low-energy ligand-to-metal charge-transfer transition which is directly associated with the presence of the noninnocent ligand H_2bihyat. Efforts to synthesize molybdenum(VI) and uranium(VI) compounds are underway taking advantage of the high ability of the ligand H_2bihyat to stabilize high oxidation states.

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