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Vanadium(V) Compounds with the Bis-(hydroxylamino)-1,3,5-triazine Ligand, H_2bihyat: Synthetic, Structural, and Physical Studies of $[V_2^VO_3(bihyat)_2]$ and of the Enhanced Hydrolytic Stability Species *cis*-$[V^VO_2(bihyat)]^-$

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Reaction of the ligand 2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazine (H_2bihyat) with NaV^VO_3 in aqueous solution followed by addition of either Ph_4PCl or $C(NH_2)_3Cl$, respectively, gave the mononuclear vanadium(V) compounds $Ph_4P[V^VO_2(bihyat)]\cdot 1.5H_2O$ **(1)** and $C(NH_2)_3[V^VO_2(bihyat)]$ **(2)**. Treatment of $V^{IV}OSO_4\cdot 5H_2O$ with the ligand H_2bihyat in methyl alcohol under specific conditions gave the oxo-bridged dimer $[V^V_2O_2(\mu_2\text{-}O)(bihyat)_2]$ **(3).** The structures for **1** and **3** were determined by X-ray crystallography and indicate that these compounds have distorted square-pyramidal arrangement around vanadium. The ligand bihyat^{2-} is bonded to vanadium atom in a tridentate fashion at the pyridine-like nitrogen atom and the two deprotonated hydroxylamino oxygen atoms. The high electron density of the triazine ring nitrogen atoms, which results from the resonative contribution of electrons of exocyclic nitrogen atoms (Scheme 4), leads to very strong V−N bonds. The *cis*-$[V^VO_2(bihyat)]^-$ species exhibits high hydrolytic stability in aqueous solution over a wide pH range, 3.3−11.0, as it was evidenced by ^{1}H and ^{51}V NMR spectroscopy and potentiometry. The high affinity of the H_2bihyat ligand for the $V^VO_2^+$ unit, its tridentate character, as well as its small size, paves the way for potential applications in medicine, analysis, and catalysis for the $C(NH_2)_3[V^VO_2(bihyat)]$ compound. The molecular structures, vibrational and electronic spectra, and the energetics of the metal−ligand interaction for compounds **1** and **3** have been studied by means of density functional calculations.

Introduction

Vanadium has been recognized as an important trace element with biological[1,2] and pharmacological activity.[3,4] Both inorganic and organic vanadium compounds have been shown to lower plasma glucose and lipid levels, increase peripheral glucose uptake, improve insulin resistivity, and normalize liver enzyme activities in a variety of animal models of both type I and II diabetes.[5,6] Consequently, several vanadium-containing compounds, that have been tested in vitro or in vivo, appear as very promising insulin-mimetic active oral drugs.[7,8] The evidence of the biological role of vanadium in vanadate-dependent haloperoxidases and vanadium−nitrogenases is also well documented.[9] A great number of vanadium compounds with different ligands have been studied as functional and structural models of this type of enzymes.[10]

Water-soluble mononuclear vanadium compounds have been the subject of intense interest in recent years.[11] One general feature common to most vanadium(IV/V) compounds

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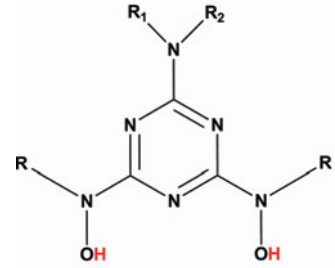
is their hydrolytic instability because of the highly oxophilic nature of vanadium in the oxidation states IV and V. Therefore, in aqueous solution, hydroxide groups replace ligands, followed by the formation of oxo-bridged polynuclear aggregates. Hydrolytically stable vanadium(IV/V) compounds may potentially have medicinal applications in non-insulin-dependent diabetes mellitus, which is the most common form of diabetes in adult humans,[5,6] and in anticancer therapy.[12,13] Resistance towards hydrolysis should increase with the complex thermodynamic stability. We are interested in exploring new ligand families that may produce stable complexes and investigate their hydrolysis and the relevant factors affecting it. Therefore, we searched for electron-rich oxygen based ligands that may lead to strong hard acid-base binding. More specifically, we chose a new family of hydroxylamine based ligands (H_2bht) shown in Scheme 1, knowing that vanadium has a great affinity for hydroxylamino substituted derivatives.[14] The attachment of hydroxylamino groups to the electron poor 1,3,5-triazine ring

Scheme 1



H_2bht

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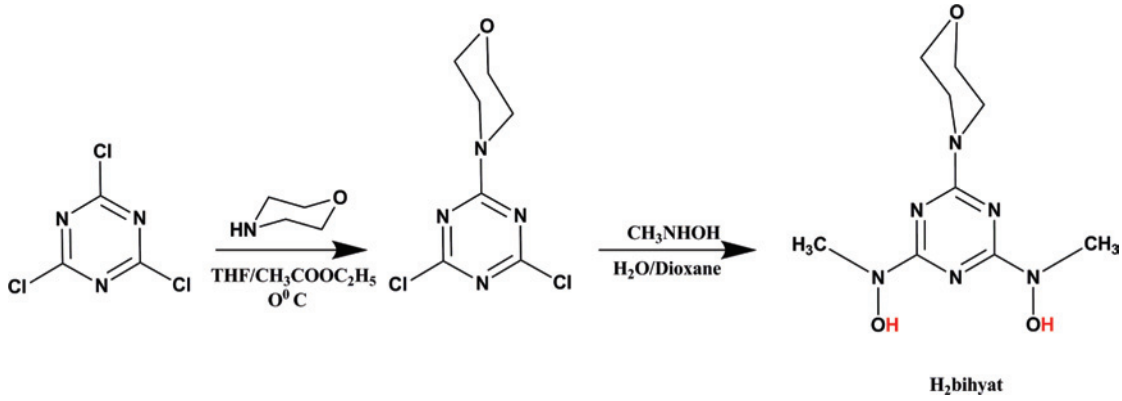
Scheme 2



H_2bihyat

provides a number of advantages that are critical for strong ligation: (i) a dramatic increase in the stability of hydroxyamino groups to oxidation; (ii) easy *O*-deprotonation of hydroxyamino group; and (iii) the participation of the nitrogen atom, at position 1 of the 1,3,5-triazine cycle, in addition to the two deprotonated hydroxylamino oxygen atoms in the binding with metal cations, makes these ligands suitable for tridentate ligation. Moreover, the ability to tune the electronic properties of this class of ligands by simply changing the *R*-groups (Scheme 1) is of vital importance for the modification of complexation constants and hydrophobicity of the vanadium-H_2bht complexes. The synthesis and crystal structure has been recently reported of an iron(III)[15] and of a titanium(IV)[16] compound with this class of ligands as well as the synthesis and crystal structure of an ethylene-bridged H_2bht-titanium(IV) compound, $[Ti^{IV}_2(OR)_4(bht)]$.[17] All these Fe^{III} and Ti^{IV}-bht complexes have high hydrolytic stability.

With the goal to prepare hydrolytically stable vanadium compounds and anticipating that incorporation of H_2bht ligands to vanadium would lead to such vanadium compounds, we embarked on an effort to prepare vanadium complexes with the ligand 2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazine (H_2bihyat) shown in Scheme 2. Herein, we report on the synthesis, structural, and physicochemical characterization of the vanadium(V)-bihyat^{2-} compounds. The results (multinuclear NMR and potentiometry) show that the mononuclear species *cis*-$[V^VO_2(bihyat)]^-$ exhibits hydrolytic stability in aqueous solution at a wide range of pHs, 3.3−11. In addition, its single negative charge helps its transport[18] in biological systems and thus makes it a promising candidate for medicinal applications. Density functional calculations have been carried out for compounds **1** and **3** to examine the nature and strength of the metal−ligand interaction, as well as to elucidate their vibrational and electronic spectra.

Experimental Section

Materials. $V^{IV}OSO_4 \cdot 5H_2O$ (96%) and Ph_4PCl (97%) were purchased from Merck. $NaVO_3$ (99.9%) and guanidinium chloride (98%) were purchased from Aldrich. Merck silica gel 60F254 TLC plates were used for thin layer chromatography. 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.

2,6-Bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazine (H_2bihyat). The ligand was prepared by the literature procedure[15a] and recrystallized twice with isopropyl alcohol. Its purity was confirmed by elemental analysis (C, H, and N), infrared spectroscopy and melting point, ^{1}H and ^{13}C NMR. $R_f = 0.51$ ($CH_3COOOC_2H_5$/CH_3OH 4:1).

Tetraphenylphosphonium [2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5- triazinato-O,O,N]-*cis*-dioxovanadate(V), $Ph_4P[V^VO_2(bihyat)] \cdot 1.5H_2O$ (1). Solid H_2bihyat (0.070 g, 0.27 mmol) was added in one portion to a stirred solution of NaV^VO_3 (0.033 g, 0.27 mmol) in deoxygenated water (5 ml) at ambient temperature (∼20 °C). Upon dissolution of the ligand the colorless solution of NaV^VO_3 turned to orange. The pH of the solution was 6.5. To this solution was added tetraphenylphosphonium chloride (0.110 g, 0.29 mmol), and the reaction mixture was stirred for 10 min. The solution was filtered and left in air to crystallize at room temperature (∼20°C) for 1 day to get 0.099 g of yellow crystals of $Ph_4P[V^VO_2(bihyat)] \cdot 1.5H_2O$ (yield 52%, based on vanadium). IR (KBr) 3467 (m), 3064 (w), 2965 (w), 2916 (w), 2884 (w), 2851 (m), 1648 (s), 1579 (vs). 1540 (vs), 1503 (s), 1437 (vs), 1396 (m), 1364 (w), 1321 (m), 1270 (s), 1201 (w), 1165 (m), 1108 (vs), 1022 (m), 997 (m), 922 (vs), 908 (vs), 857 (w), 820 (w), 758 (m), 723 (vs), 691 (s), 601 (m), 526 (vs), 430 (w). Elemental analysis calcd (%) for $C_{33}H_{37}N_6O_{6.5}PV$ (703.56): C, 56.34; H, 5.31; N, 12.09; V, 7.24. Found: C, 56.35; H, 5.30; N, 11.95, V, 7.09.

Guanidinium [2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazinato-O,O,N]-*cis*-dioxovanadate(V), $C(NH_2)_3[V^VO_2(bihyat)]$ (2). The compound was prepared by the same method as used for the synthesis of $Ph_4P[V^VO_2(bihyat)] \cdot 1.5H_2O$, except that guanidinium chloride was used instead of tetraphenylphosphonium chloride to get the complex in 55% yield (based on vanadium). Compound **2** precipitated out immediately upon addition of the guanidinium chloride. Crystals of **2** suitable for X-ray structure analysis were obtained by vapour diffusion of acetone into a concentrated aqueous solution of it. IR (KBr) 3376 (m), 3200 (w),

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2965 (w), 2863 (w), 1661 (vs), 1575 (w), 1548 (s), 1508 (m), 1447 (m), 1405 (w), 1369 (w), 1319 (m), 1271 (m), 1206 (w), 1163 (w), 1111 (m), 1026 (m), 948 (m), 902 (vs), 767 (w), 743 (w), 672 (w), 606 (m), 528 (w), 432(w). Elemental analysis calcd (%) for $C_{10}H_{20}N_9O_5V$ (397.27): C, 30.23; H, 5.07; N, 31.73; V, 12,82. Found: C, 30.29; H, 4.90; N, 32.15; V, 12.53.

***μ_2*-Oxo-bis{2,6-bis[hydroxy(methyl)amino]-4-morpholino-1,3,5-triazinato-O,O,N} Oxovanadium(V), $[V^V_2O_2(\mu_2\text{-}O)(bihyat)_2]$ (3).** Solid H_2bihyat (0.125 g, 0.49 mmol) was added in one portion to a stirred solution of $V^{IV}OSO_4 \cdot 5H_2O$ (0.125 g, 0.49 mmol) in deoxygenated methyl alcohol (35 ml) at 35 °C. Upon addition of the ligand the blue color of the solution turned to light brown, and when the whole quantity of it dissolved the color of the solution changed to deep brown. The reaction mixture was stirred overnight at ~20°C and then, it was filtered and left in air to crystallize at room temperature (~20°C). The deep blue crystals of **3** were formed from this solution after 5 days. Yield: 65 mg (10% based on vanadium). IR (KBr) 3425 (w), 2967 (w), 2917 (w), 2850 (w), 1642 (s), 1549 (vs), 1490 (s), 1437 (m), 1401 (m), 1365 (w), 1331 (w), 1298 (w), 1276 (m), 1197 (w), 1166 (w), 1113 (m), 1068 (w), 1027 (m), 977 (vs), 949 (w), 856 (w), 768 (m), 740 (m), 647 (w), 623 (m), 595 (m), 526 (w), 458 (w), 434 (w). Elemental analysis calcd (%) for $C_{18}H_{28}N_{12}O_9V_2$ (658.42): C, 32.84; H, 4.29; N, 25.53; V, 15.47. Found: C, 32.92; H, 4.18; N, 25.61; V, 15.61.

NMR Spectroscopy and Sample Preparation. NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz, 75.5 MHz, and 78.9 MHz for ^{1}H,^{13}C, and ^{51}V nuclei, respectively. The ^{1}H, ^{13}C, and ^{51}V NMR spectra were recorded using a sweep width of 1000, 4500, and 30.000 Hz, respectively and a 30° pulse. For the ^{1}H and^{13}C NMR experiments in organic solvents as reference was used TMS (tetramethylsilane), while in aqueous solutions tert-butanol as external reference. For the ^{51}V NMR experiments a solution of $VOCl_3$ in $CDCl_3$ was used as an external reference. The 2D ^{1}H NMR COSY-45 (pulse sequence 90°-t_1-45°) experiments were conducted using 256 increments (each consisting of 16 scans) covering the full spectrum (4.0 ppm in both dimensions). The phase sensitive HMQC sequence enriched with BIRD filter and GARP decoupling (90°) was applied at inverse H, C correlation for the 2D HMQC spectra. The standard NOESY pulse sequence (90°-t_1-90°-t_m-90°) was used in the 2D {^{1}H} EXSY-NOESY measurements and these spectra were acquired using 512 increments (with 16 scan each) covering the full spectrum (4.0 ppm in both dimensions) and 0.20−0.35 s mixing time (t_m).

The samples were prepared by dissolving crystalline material in the appropriate solvent ($CDCl_3$, CD_2Cl_2, CD_3CN, or D_2O) just prior to the NMR experiment. The hydrolytic and redox stability of **2** in D_2O, with time in each pH, was examined by acquiring the ^{1}H NMR spectra, immediately and 24 h after the pH adjustment of the samples. The ^{1}H NMR spectra 24 h after the adjustment of the pH (pHs from 1.5 to 11.0) were identical with the spectra obtained at zero time indicating that the composition of the solutions remained stable. The stability experiments with 2,6-pyridinedicarboxylic acid (H_2dipic) were performed in stable ionic strength in the presence of 0.40 M KCl. The solutions were left for half an hour to equilibrate prior to the experiment. The pH was adjusted with dilute solution of DCl or NaOD in D_2O, and the pH was checked prior to and after the experiment.

X-ray Crystallography. Intensity data for the compounds **1** and **3** respectively were measured employing an XCalibur III 4-cycle diffractometer, equipped with a CCD camera detector, using a monochromatized Mo Kα ($\lambda = 0.7107$ Å) radiation at 100 K. In both cases, analytical absorption corrections were applied. The structures were solved by direct methods using the program SHELX-86[19] and refined on F^2 by a full-matrix least-squares procedure with anisotropic displacement parameters for all the non-hydrogen atoms based on all data minimizing $wR = \sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^2]^{1/2}$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, and GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.[19] A summary of the relevant crystallographic data and the final refinement details are given in Table 1. The positions of hydrogen atoms were calculated from stereochemical considerations and kept fixed isotropic during refinement or found in a DF map and refined with isotropic thermal parameters. Crystallographic diagrams were drawn using the ORTEP-3[20] software package at 50% probability level. The quality of the crystals of compound **2** was poor to allow us to solve the structure.

Table 1. Summary of X-Ray Crystallographic and Experimental Data for the Compounds **1** and **3**

parameter	**1**	**3**
composition	$C_{66}H_{76}N_{12}O_{14}P_2V_2$	$C_{18}H_{28}N_{12}O_9V_2$
formula wt.	1425.36	658.40
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	13.1164(16)	10.684(3)
b, Å	16.8622(11)	10.8326(18)
c, Å	16.9807(8)	12.759(3)
α, deg	76.311(5)	76.914(17)
β, deg	67.911(7)	69.12(2)
γ, deg	67.791(9)	74.516(18)
V, Å^3	3202.2(5)	1315.4(5)
D_{calc}, Mg m^{-3}	1.478	1.662
temp, K	100	100
λ(Mo Kα), Å	0.71073	0.71073
Z	2	2
F(000)	1488	676
θ range for data collection (deg)	3.31−30.55	3.10−30.48
μ mm^{-1}	0.420	0.783
reflections collected/ unique	50279/17719	16868/6730
R_{int}/ GOF on F^2	0.0330/1.145	0.0931/0.970
data/ restraints/ parameters	17719/0/930	6730/0/370
$R1(F_o)$, $wR2(F_o)$ $[I \geq 2\sigma(I)]$	0.0725, 0.2326	0.0708, 0.1431
$R1(F_o^2)$, $wR2(F_o^2)$ (all data)	0.1048, 0.2542	0.2874, 0.1886

Potentiometry. All measurements were made in water. The purity of the ligand H_2bihyat was checked pH-potentiometrically and the exact concentration of the solutions was determined by the Gran method.[21] The concentration of H_3O^+ in the stock solutions was determined by pH-potentiometry. The vanadium(V) stock solution was prepared by dissolving KV^VO_3 in KOH solution of known molarity, and its H_3O^+ concentration was calculated. The ionic strength was adjusted to 0.20 M KCl and the temperature was 25.0 ± 0.1 °C. The stability constants of the proton and vanadium(V) complexes ($[HV^VO_4]^{2-}$ considered as component) were determined by pH-potentiometric titration of 10.0 mL samples. The concentrations of the ligand were 0.001, 0.002, or 0.004 M, and the metal ion to ligand molar ratios were 0:1, 0:2, 0:4, 1:1, 1:2, or 1:4. Titrations were first performed with KOH solutions of known concentrations (ca. 0.4 M). However, these titrations were not reproducible and could not be evaluated because of the slow decomposition of the polyoxoanions of vanadium(V) or other formed oligomeric species. For this reason, back titrations were performed with HCl solution of known concentration (ca. 0.2 M) over the pH range 11.7−2.5 to avoid the formation of the kinetically inert decameric vanadium(V) oxoanionic species. All titrations were

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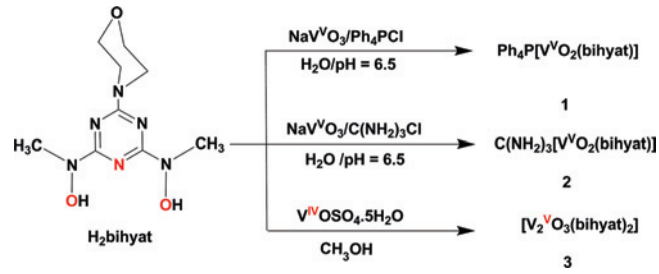
carried out under purified argon atmosphere to avoid interference from the oxygen and carbon dioxide. At ligand concentration 0.004 M, the neutral form of the ligand $[H_2bihyat]^0$ precipitated at pH ~ 6.5 because of its low solubility, and thus, in this case points at pH > 6 were omitted from the calculation. The reproducibility of the titration curves used in the calculations was within 0.005 pH unit throughout the whole pH range. For potentiometric titrations, an automatic titration set including a Dosimat 665 autoburette, an Orion 710A precision digital pH-meter, and an IBM-compatible personal computer was used. A Metrohm 6.0234.100 semimicro combined glass electrode was calibrated for hydrogen ion concentration according to the method of Irving et al.[22] The pK_w calculated from strong acid-strong base titration was 13.755 ± 0.010. The concentration stability constants, $\beta_{pqr} = [M_pL_qH_r]/([M]_p[L]_q[H]_r)$, were calculated with the aid of the PSEQUAD[23] computer program. The stability constants of the polyacid formation equilibria of $[HV^VO_4]^{2-}$ were taken from the literature[24] and were corrected for ionic strength using the Davies equation.

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.[25]

Computational Details. The electronic structure and geometries of the compounds **1** and **3** studied were computed within the density functional theory using gradient corrected functionals, at the Becke3LYP computational level[26] using the Gaussian-03 package.[27] The effective core potential (ECP) approximation of Hay and Wadt was used for describing the $(1s^22s^22p^6)$ core electron for vanadium whereas the associated double-ζ quality basis sets were used for the valence shell.[28] The 6-311(G) basis set used for the remaining atoms.[29] Time-dependent density functional theory (TD-TFT)[30−32] calculations were performed employing the same functional and basis set for the analysis of the excitation energies for both compounds. The energy partitioning analysis (EPA)[30] based upon the energy decomposition analysis developed independently by Morokuma[31] and by Ziegler and Rauk[32] was carried out for the anion of **1**, *cis*-$[V^VO_2(bihyat)]^-$, on a molecular geometry fully optimized with the ADF package[33] at the BP86 level[34] using uncontracted Slater orbitals (STOs)[35] with triple-ζ quality in the valence region and double-ζ quality in the core region augmented by one set of polarization function (TZP). Relativistic effects were accounted for by the zero order regular approximation (ZORA).[36] The $(1s^2)$ core electrons of carbon, oxygen, and nitrogen and the $(1s^22s^22p^63s^23p^6)$ of vanadium were treated by the frozen core approximation.[37] The geometry optimizations at both levels were performed without any symmetry constraint followed by frequency calculations to confirm that a real minimum had been reached. The final optimized molecular structures of the anion of **1** and **3** have nearly C_s and C_2 symmetries, respectively. Harmonic vibrational frequencies reported here were determined at the B3LYP level by the analytical evaluation of second derivatives of the energy with respect to nuclear displacement and were scaled by 0.9614.[38]

Scheme 3



Results and Discussion

Synthesis. Synthesis of the bis(hydroxyamino)triazine ligand H_2bihyat was based on facile nucleophilic substitution at the 1,3,5-triazine ring (Scheme 2). At this point, it is worth noting that the high purity of the ligand H_2bihyat was of vital importance to get compounds **1**−**3**. Thus, the ligand was recrystallized twice from isopropanol. It is well known[39] that the hydroxylamines are redox active ligands, and the preparation of their vanadium(V)-compounds[39] is very sensitive to temperature, purity, and concentration of the ligand. In our case, the presence of impurities into the ligand H_2bihyat, which might be hydroxylamine derivatives, presumably, lead the reaction to another route. Compounds **1**−**3** were prepared according to Scheme 3. The mononuclear complexes **1** and **2**, were synthesized by sequential treatment of NaV^VO_3 with H_2bihyat (eq 1) and then with Ph_4PCl and $C(NH_2)_3Cl$ to get **1** and **2** respectively at pH 6.5.

$$[H_2V^VO_4]^- + H_2bihyat \rightarrow cis\text{-}[V^VO_2(bihyat)]^- + 2H_2O \quad (1)$$

Compound **3** was prepared by reacting $V^{IV}OSO_4 \cdot 5H_2O$ with the ligand H_2bihyat in methyl alcohol at 35 °C and under inert atmosphere at the beginning (12 h) and then

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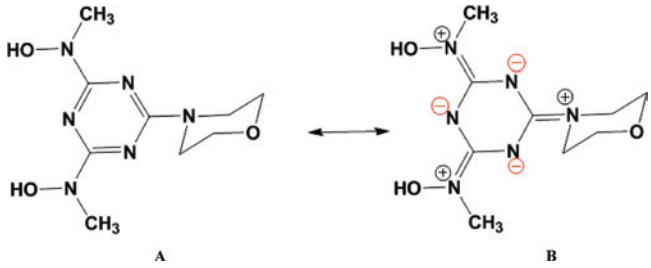
Scheme 4



exposure to air (eq 2) at ambient temperature (~20 °C) for 5 days.

$$2V^{IV}OSO_4 + 2H_2bihyat + \frac{1}{2}O_2 \rightarrow [V_2^{V}O_2(\mu_2\text{-}O)(bihyat)_2] + 2H_2SO_4 \quad (2)$$

From the sequence of the color changes of the solution during the synthesis, brown, dark yellow-brown, black, and finally dark blue, one might guess that at first the species "$V^{IV}O$-(bihyat)" is formed which is unstable and is oxidized to get compound **3**. The case is under further investigation with electron paramagnetic resonance measurements and electrospray ionization-mass spectrometry. The synthesis of **3** in a crystal form suitable for X-ray structure analysis cannot be achieved if the temperature of the reaction is ~20 °C.

Crystal Structures. The molecular structure of the anion of the compound **1** is shown in Figure 1. A selection of interatomic distances and bond angles relevant to the vanadium coordination sphere in **1** is listed in Table 2. The vanadium atom has a distorted square pyramidal geometry and is bonded to a tridentate bihyat^{2-} ligand at the pyridine-like nitrogen atom and the two deprotonated hydroxyamino groups as well as two oxo groups [O(3)] and [O(4)]. The two largest angles about the vanadium atom are O(1)−V(1)−O(2) = 145.52(12)° and O(4)−V(1)−N(1) = 135.72(17)°, and these angles are used to define $\tau = (145.52 - 135.72)/60 = 0.163$. Since the τ value is closer to 0 than to 1, the geometry for this vanadium species is approaching square-pyramidal. At this point, it is worth noting that the V−N_{py} bond distance of 1.993(3) Å is indicative of a very strong bond of the pyridine-like nitrogen to vanadium and constitutes the shortest V−N_{py} distance so far reported for vanadium compounds. The dipicolinate analogue of **1**, *cis*-

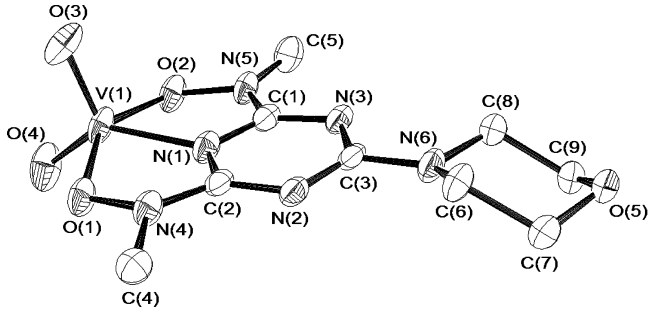


Figure 1. ORTEP representation of the anion of compound **1** at 50% probability ellipsoids giving atomic numbering.

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

	1		
parameter	molecule 1	molecule 2	**3**
V(1)−O(1)	1.974(3)	1.981(4)	1.915(5)
V(1)−O(2)	1.994(4)	1.988(4)	1.903(5)
V(1)−O(3)	1.624(3)	1.629(3)	1.605(4)
V(1)−O(4)	1.637(3)	1.636(4)	1.775(5)
V(1)−N(1)	1.993(3)	1.990(3)	1.966(5)
V(2)−O(4)			1.785(4)
V(2)−O(6)			1.922(4)
V(2)−O(7)			1.904(5)
V(2)−O(8)			1.980(5)
O(1)−V(1)−O(2)	145.52(12)	147.74(13)	148.90(18)
O(1)−V(1)−O(3)	102.12(15)	100.3(2)	98.2(2)
O(1)−V(1)−O(4)	97.59(17)	98.23(17)	99.3(2)
O(1)−V(1)−N(1)	74.27(14)	74.59(13)	74.9(2)
O(2)−V(1)−O(3)	102.38(16)	100.9(2)	98.3(2)
O(2)−V(1)−O(4)	95.83(17)	96.15(16)	100.1(2)
O(2)−V(1)−N(1)	73.96(14)	74.06(13)	74.2(2)
O(3)−V(1)−O(4)	111.06(19)	111.7(2)	108.7(2)
O(3)−V(1)−N(1)	113.21(16)	118.09(18)	128.0(2)
O(4)−V(1)−N(1)	135.72(17)	130.20(17)	123.2(2)
V(1)−O(4)−V(2)			128.3(2)
O(4)−V(2)−O(6)			99.51(19)
O(4)−V(2)−O(7)			98.2(2)
O(4)−V(2)−O(8)			109.8(2)
O(4)−V(2)−N(7)			123.0(2)
O(6)−V(2)−O(7)			148.1(2)
O(6)−V(2)−O(8)			98.1(2)
O(6)−V(2)−N(7)			74.2(2)
O(7)−V(2)−O(8)			98.2(2)
O(7)−V(2)−N(7)			.1(2)
O(8)−V(2)−N(7)			127.2(2)

Table 3. Bond Angles (deg) Indicating Planarity of out-of-ring Nitrogen Atoms of the Ligand Bihyat^{2-}

C(3)−N(6)−C(6)	120.3	C(2)−N(4)−O(1)	115.2	C(1)−N(5)−O(2)	114.6
C(3)−N(6)−C(8)	121.4	C(2)−N(4)−C(4)	127.0	C(1)−N(5)−C(5)	128.0
C(6)−N(6)−C(8)	113.8	O(1)−N(4)−C(4)	116.2	O(2)−N(5)−C(5	17.4
sum	355.5		358.4		360.0

$[V^{V}O_2(dipic)]^-$, has a V−N_{py} bond length of 2.096 Å.[40] Such a short V−N bond distance was only reported for vanadium(V) compounds containing V−N_{amide} bonds.[40b−d] To give a reasonable explanation for this very short V−N_{py} bond distance we examined very carefully the ligand and two structural features emerged, more specifically (i) the aromatic ring of the triazine moiety is a highly twisted hexagon, where all the C−N−C angles are around 115° and all N−C−N angles are around 125°; for example, a C(2)−N(2)−C(3) angle of 113.13° and a N(1)−C(2)−N(2) angle of 124.2°, and (ii) highly planar array of the body of the ligand including all six nitrogens, the inner ring, as well as out-of-ring nitrogen atoms; this may be confirmed by the sum of bond angles of nearly 360° surrounding the out-of-ring nitrogen atoms (Table 3). These two features are all in agreement with a large contribution of the resonative structure "B" presented in Scheme 4, according to which all out-of-ring nitrogen atoms are of approximately sp^2 config-

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uration, while the inner ring nitrogen atoms, including the one ligated to vanadium, possess high electron densities. Therefore, a strong electron donation from the ring nitrogen atom to vanadium takes place and this results in a very strong V−N bond.

The molecular structure of compound **3** is shown in Figure 2. Selected metrical parameters of **3** are given in Table 2. The two halves of **3**, bridged by an oxygen atom O(4), have exactly the same coordination environment though there are slight differences in the corresponding bond lengths and angles. The trigonality index, τ, is 0.348 for both V(1) and V(2), and this implies that the square pyramidal geometry for both vanadium(V) atoms is distorted towards trigonal prismatic geometry. Each vanadium atom of the two halves is bonded to a tridentate bihyat^{2-} ligand at the pyridine-like nitrogen atom, and the two deprotonated hydroxyamino groups as well as a μ_2-bridging oxo group and an oxo ligand. The $V_2O_3^{4+}$ core of **3** exhibits a twisted syn-angular structure with the dihedral angle defined by the O(3)−V(1)−O(4) and O(8)−V(2)−O(4) planes to be equal to 24.7(3)°. The V(1)−O(4)−V(2) angle [128.3(3)°] is in the range from 100 to 170° that have been observed for other $V_2O_3^{4+}$ cores. The V−O−V angle has been found to be dependent on the geometry of the core with the syn-angular geometries to exhibit small angles versus the almost linear V−O−V anti-angular geometries.[41] There are few exceptions in the above trend which have been assigned to the steric interactions between the two bridged components. The small angle observed for **3** is in agreement with the syn-angular configuration of the complex.

NMR Spectroscopy. The ^{51}V NMR spectra of **1**, that is, $Ph_4P[V^VO_2(bihyat)]\cdot 1.5H_2O$ and **3**, that is, $[V^V_2O_2(\mu_2\text{-}O)(bihyat)_2]$, compounds in $CDCl_3$ gave peaks at −485 and −422 ppm, respectively. In addition, compound **3** gave also a small peak at −187 ppm which was absent from the ^{51}V NMR spectra of the compound in other solvents such as CD_2Cl_2 and CD_3CN. The peak at −187 ppm might be due to a slight decomposition of **3** in $CDCl_3$. The case is under further investigation. These chemical shifts are close to those expected for five-coordinate vanadium(V) compounds with electronegative donor atoms (i.e., nitrogen and oxygen atoms).[42] The ^{51}V NMR spectrum of **2**, that is, $C(NH_2)_3[V^VO_2(bihyat)]$, in D_2O in the pH range 3.3 to 11 exhibits one peak at −502 ppm which is close to the chemical shift observed for other five-coordinate vanadium(V) compounds with the same donor atoms (4O, N), such as *cis*-$[V^VO_2(dipic)]^-$ which gives a signal at −518 ppm[7a] at pH values lower than 6.

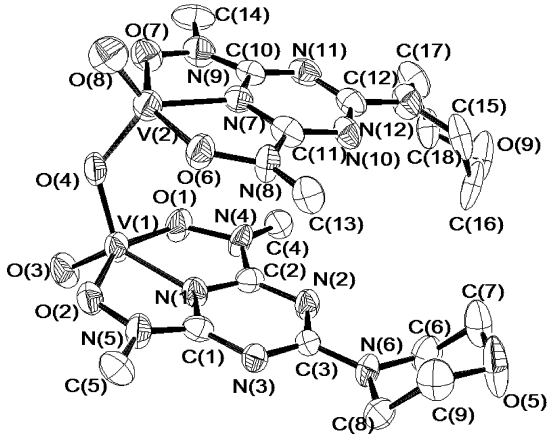


Figure 2. ORTEP representation of the compound **3** at 50% probability ellipsoids giving atomic numbering.

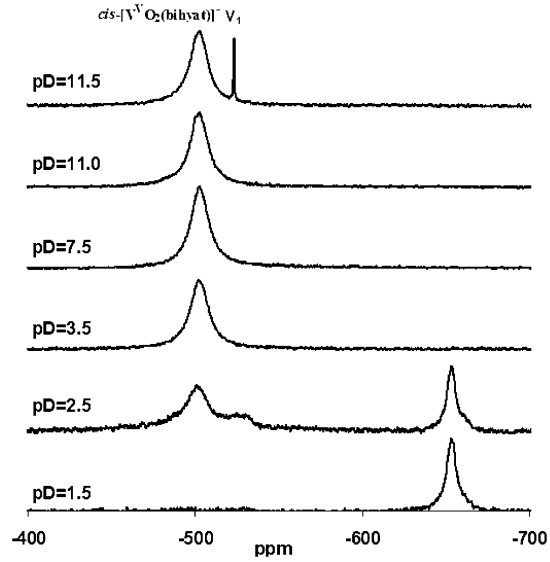


Figure 3. ^{51}V NMR spectra of a D_2O solution containing 0.01 M of $C(NH_2)_3[V^VO_2(bihyat)]$ in the pD range 1.5 to 11.5. The pDs of these solutions have been adjusted with diluted D_2O solution of NaOD and DCl.

Metal ligation induces a significant shift (1.26 to 4.36 ppm) in the ^{13}C NMR peaks (Supporting Information, Table S1) of the triazine ring carbon atoms for the vanadium compounds **1**−**3** to lower field in comparison to the corresponding peaks of the free ligand. In contrast, the ^{13}C NMR peaks of the methyl groups exhibit only a small shift (0.29−1.97 ppm) to higher field in accordance with the non-ligation of the nitrogen atom of the $-N(CH_3)O^-$ group to vanadium. This is also in line with the small (0.06−0.17 ppm) shift of the methyl protons in the ^{1}H NMR spectra (Supporting Information, Table S1) of the compounds **1**−**3**.

Compound **2** is very stable in the pH range 3.3−11, in marked contrast to its dipicolinate analogue, *cis*-$[V^VO_2(dipic)]^-$, which is stable only in acidic pH below 6. At pH above 11, a slight decomposition of **2** was observed, and a sharp signal for vanadate also appeared in the ^{51}V NMR spectra (Figure 3). However, even at pH above 11, solutions of **2** (10 mM) revealed less than 10% decomposition. ^{1}H and ^{13}C NMR spectra showed the appearance of the peaks of the free ligand, in addition to the peaks of **2**, and thus, it is clear that its decomposition is due to hydrolysis of it at high pH values. At pH below 3.3, new species were formed in solution as it was evidenced by NMR spectroscopy. In particular, the ^{51}V NMR spectrum of **2** at pH = 2.5 (Figure 3)

(41) (a) Chatterjee, P. B.; Bhattacharya, S.; Audhya, A.; Choi, K. Y.; Endo, A.; Chaudhury, M. *Inorg. Chem.* **2008**, *47*, 4891–4902. (b) Schmidt, H.; Bashirpoor, M.; Rehder, D. *Dalton Trans.* **1996**, 3865–3870. (c) Dutta, S.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1993**, *32*, 5343–5348. (d) Mondal, B.; Ghosh, T.; Sutradhar, M.; Mukherjee, G.; Drew, M. G. B.; Ghosh, T. *Polyhedron* **2008**, *27*, 2193–2201.

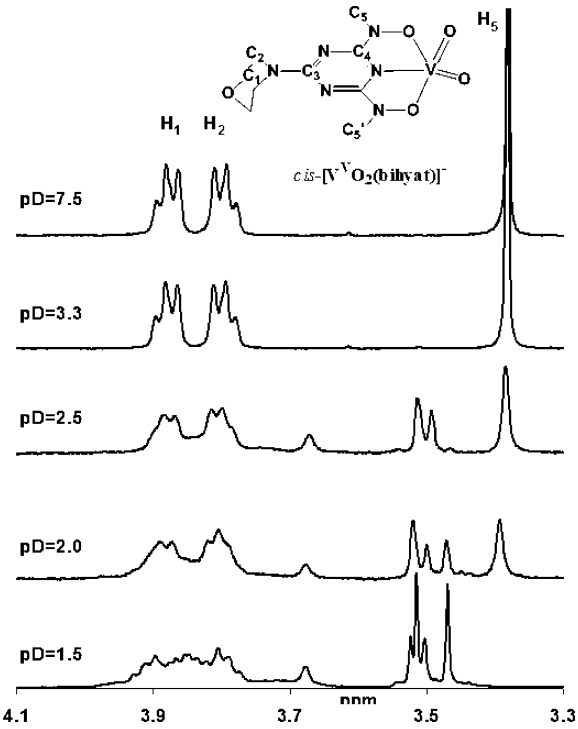


Figure 4. ^{1}H NMR spectra of a D_2O solution containing 0.01 M of $C(NH_2)_3[V^VO_2(bihyat)]$ in the pD range 1.5 to 7.5. The pDs of these solutions have been adjusted with diluted D_2O solution of NaOD and DCl.

showed one broad peak at ~−530 ppm and a sharper peak at −653 ppm in addition to the peak at −502 ppm. At pH 1.5 the upfield peak at −653 ppm is the only one present, and it was assigned to a vanadate species containing one side-on chelate hydroxylamine.[39] The ^{51}V and the ^{1}H NMR peaks did not show any broadening at pH below 3.3, and this means that there are not any paramagnetic vanadium(IV) species present in solution. Increment of the pH back to 7.0 does not restore compound **2** in solution, and this simply means that the ligand was decomposed in the acidic environment. The ^{1}H NMR spectrum of the aqueous solution of **2** at pH 2.5 (Figure 4) showed three additional peaks between 3.45 and 3.70 ppm, in comparison to the ^{1}H NMR spectrum of **2** at pH 3.5 (Figure 4), which were assigned to the methyl protons of *N*-methylhydroxylamine (Hmethy) and of the coordinated ligand bihyat^{-2} (Figure 4). Thus, the ^{51}V NMR signal at −653 ppm and the three peaks in the ^{1}H NMR (Figure 4, pH 2.5) were assigned to the compound $[V^VO(CH_3NHO)(bihyat)]$. The *N*-methylhydroxylamine (CH_3NHOH) is presumably a decomposition product of the ligand H_2bihyat. To confirm this hypothesis, the ^{51}V and ^{1}H NMR spectra of an aqueous solution (pH 4) containing compound **2** and *N*-methylhydroxylamine ($C_2 > C_{Hmethy}$) were recorded. The solution presumably contains compounds **2** and $[V^VO(CH_3NHO)(bihyat)]$ (**4**). Compound **4** is formed from the reaction of **2** with CH_3NHOH according to eq 3:

$$C(NH_2)_3[V^VO_2(bihyat)] + CH_3NHOH \rightarrow [V^VO(CH_3NHO)(bihyat)] + C(NH_2)_3OH \quad (3)$$

The ^{51}V NMR spectrum of the above mentioned solution showed two peaks at −502 and −653 ppm due to compounds **2** and **4**, respectively (Figure 5a), and its ^{1}H NMR spectrum showed four peaks due to methyl protons at 3.40, 3.48, 3.52, and 3.67 ppm which were assigned to H(5) of bihyat^{2-} in **2**, to H(5) and H(5′) of bihyat^{2-} in **4**, and to H(6) of methy$^-$ bound to a side on fashion to vanadium atom in **4**, respectively (Figure 5b). A comparison of the ^{1}H NMR and ^{51}V NMR spectra shown in Figures 3 (pH = 2.5), 4 (pH =2.5), and 5 reveals that the compound produced from the decomposition of **2** at pH ≤ 2.5 is compound **4**, and its structure is shown in Figure 5. One of the outstanding properties of **2** is its high hydrolytic stability in aqueous solution. Even at 10 μM concentration of **2** in water, no formation was not observed of free vanadate or free ligand in the pH range 3.3 to 11.0 by ^{51}V and ^{1}H NMR spectroscopy. The ability of the ligand H_2bihyat to bind vanadium(V) was compared with that of H_2dipic by ^{51}V NMR spectroscopy. The equilibrated ^{51}V NMR spectra of **2** mixed with various quantities of H_2dipic in D_2O at pH = 5.0 are shown in Figure 6. The calculated molar ratio of *cis*-$[V^VO_2(dipic)]^-$/*cis*-$[V^VO_2(bihyat)]^-$ was found to be 0.15 and 0.38 when C_2/C_{H_2dipic} equals 0.01:0.01 and 0.01:0.05,

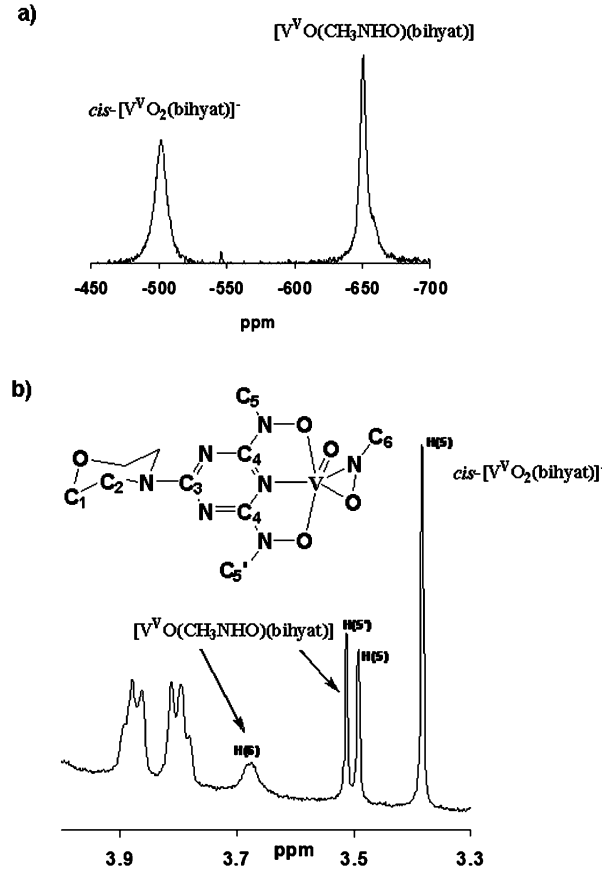


Figure 5. (a) ^{51}V NMR and (b) ^{1}H NMR spectra and assignments of a reaction mixture of $C(NH_2)_3[V^VO_2(bihyat)]$ and $(CH_3)NHOH$ with concentrations of 10 and 0.5 mM respectively at pD = 4.0 in D_2O.

(42) Rehder, D.; Weidemann, C.; Duch, A.; Priebsch, W. *Inorg. Chem.* **1988**, *27*, 584.

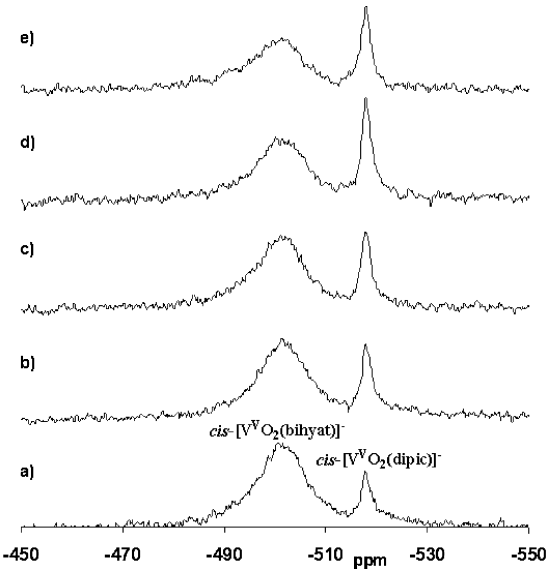


Figure 6. ^{51}V NMR spectra of D_2O solutions containing 0.01 M of $C(NH_2)_3[V^VO_2(bihyat)]$, 0.40 M KCl and (a) 0.01 M, (b) 0.02 M, (c) 0.03 M, (d) 0.04 M, and (e) 0.05 M 2,6-dipicolinic acid, respectively. The pDs of these solutions have been adjusted at pD = 5.0 with diluted D_2O solution of NaOD.

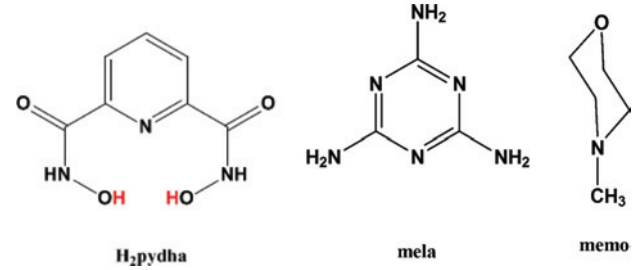
respectively. This fact reveals the higher thermodynamic stability of the vanadium(V)-bihyat^{2-} species in comparison to the vanadium(V)-dipic^{2-} species.

The ^{1}H NMR variable temperature spectra of an equimolar (0.05 M) aqueous solution of **2** and H_2bihyat did not show any peak shape change for temperatures up to 50 °C. At higher temperatures the ligand was decomposed quickly. The possibility of exchange between the coordinated and free ligand was examined by 2D {^{1}H} EXSY spectroscopy. However, no cross peaks were observed for the hydroxylamine methyl groups, at pHs 4.0, 7.0, and 10.0, at 30 and 40 °C and mixing times 100, 200, and 400 milliseconds. Apparently, the exchange rate between the free and the coordinated ligand is smaller than the time scale of this experiment. Taking into account that at similar conditions the 2D {^{1}H} EXSY spectrum of the vanadium(V)-dipicolinate complex exhibits cross peaks between the coordinated and free ligand, we conclude that the *cis*-$[V^VO_2(bihyat)]^-$ complex is more kinetically inert than its dipicolinate analogue towards ligand exchange.

Potentiometric Measurements. Acid−Base Behavior of the Ligand H_2bihyat. The p$K_{a,1}$ value of 5.32(3) for H_3bihyat$^+$ in aqueous 0.20 M KCl solution is in good agreement with the value of 5.2, in water/methanol (60:40% v/v), reported by Melman and co-workers[15a] for this monoprotonated ligand. In contrast, the p$K_{a,2}$ constant of H_2bihyat corresponding to deprotonation of a hydroxyamino group was found to be 8.25(2) in this work and differs substantially from the value of 8.8 in Melman and co-workers' work.[15a] The deprotonation of [Hbihyat]$^-$ could not be detected until pH 11.7; therefore, the p$K_{a,3}$ of this species should be higher than 12. The p$K_{a,1}$ of 5.32 for H_3bihyat$^+$ cation is close to the p$K_{a,1}$ of 5.10 for the protonated melamine (Hmela$^+$),[43] the structural analogue of the central triazine ring system of

(43) Klotz, I. M.; Askounis, T. *J. Am. Chem. Soc* **1947**, *69*, 801–803.

Scheme 5. Organic Molecules Related to the Ligand H_2bihyat



H_2bihyat (Scheme 5). In the protonated melamine (Hmela$^+$) the proton is attached to the ring nitrogen system. In addition, Melman and co-workers[15a] reported that the p$K_{a,1}$ value of H_3bihyat$^+$ is tunable by changing the *R*-groups of the morpholine moiety. Both facts support that the H^+ of H_3bihyat$^+$ can be assigned to the ring nitrogen system also. The p$K_{a,2}$ value of H_2bihyat is very similar to the p$K_{a,2}$ of 2,6-pyridinehydroxamic acid (H_2pydha)[44] (Scheme 6). The very high value for the third pK_a (>12) of Hbihyat$^-$ is most probably due to the intramolecular hydrogen bonding, and belongs to one of the −NH−OH moieties (Scheme 6). Since protonated metal complexes were not observed in the basic pH range[15a,16a] and the pK_a value of 4-methyl-morpholine (memo) is 7.41,[45] the last proton cannot be assigned to the morpholine nitrogen. The proposed structures for the various protonated forms of H_2bihyat are shown in Scheme 6.

System H_2bihyat−$[HV^VO_4]^{2-}$. Similarly to the $[H_2V^VO_4]^-$−2,6-dipicolinic acid[7a] system, one main species, the *cis*-$[V^VO_2(bihyat)]^-$ is formed in the pH range 2.5−11.5 (see Table 4). The speciation curves are depicted in Figure 7A. The amount of the free vanadium species is the smallest at pH ∼ 6.4 (Figure 7B). In addition to the major species, based on the ^{51}V-NMR measurement, which indicated new species in the acidic pH (Figure 3) to protonated compounds, *cis*-$[V^VO_2(Hbihyat)]^0$ and *cis*-$[V^VO_2(H_2bihyat)]^+$, were assumed to be formed below pH 2.5. The fitting between the experimental and calculated titration curves was significantly improved from 5.7×10^{-3} to $2.7-2.9 \times 10^{-3}$ cm^{-3} when $[V^VO_2(H_2bihyat)]^+$ was replaced in the model used by its oligomeric forms $([\{V^VO_2(H_2bihyat)\}_n]]^{n+}$ $n > 2$). The best fit was obtained with $n = 4$. However, as the formation of these species is near the lower limit of the measured pH range, it made pH measurement somewhat less accurate and thus, the stoichiometry and stability constants of these protonated species formed at pH < 2.5 should be considered as tentative values. Formation of bis-complexes could not be observed in the whole pH range. As the third p$K_{a,3}$ of the Hbihyat$^-$ is not known, a direct comparison of the stability constants of the vanadium(V) compounds formed with H_2bihyat and 2,6-dipicolinic acid was not possible. To assess the metal binding ability of the two ligands, a pH dependence of the pV_{free} values was calculated for both systems at similar conditions (C_V = 4.0 mM and H_2bihyat/M = 1). It is clear from Figure 7B that 2,6-dipicolinic acid is a weaker binder

(44) Griffith, D.; Krot, K.; Comiskey, J.; Nolan, K. B.; Marmion, C. J. *Dalton Trans.* **2008**, 137–147.
(45) Graton, J.; Besseau, F.; Berthelot, M.; Raczynska, E. D.; Laurence, C. *Can. J. Chem.* **2002**, *80*, 1375–1385.

Scheme 6. Proposed Structures of the Various Forms of the Ligand H_2bihyat

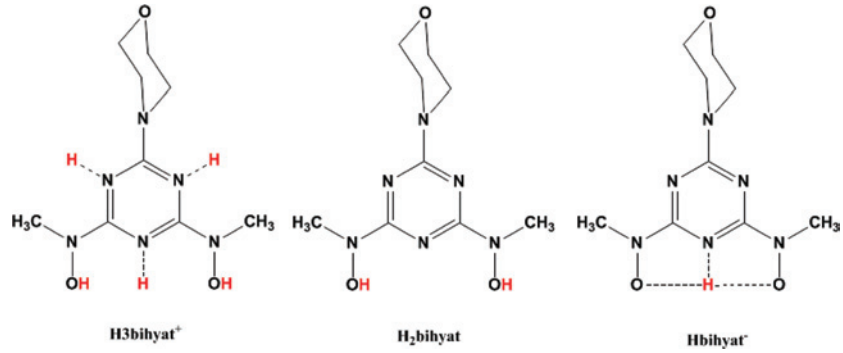


Table 4. Compositions, Notations, Formation Constants (log β), and Acidity Constants (pK_a) for H^+-Hbihyat^{2-}, H^+-mela, H^+-pydha^{2-}, H^+-memo, and $H^+-H_2V^VO_4^- -$Hbihyat$^-$[a] Systems

(p, q, r)[b]	notation	log β(± 3SD)	pK_a	reference
(2, 1, 0)	H_3bihyat$^+$	13.58 (2)	5.33	this work[c]
(1, 1, 0)	H_2bihyat[a]	8.25 (2)	8.25	this work[c]
(0, 1, 0)	Hbihyat$^-$	[...][a]	>12	this work[c]
(1, 1, 0)	Hmela$^+$	5.10 (5.02)	5.10 (5.02)	ref 42
(3, 1, 0)	H_3pydha$^+$	19.24	2.34	ref 43
(2, 1, 0)	H_2pydha	16.90	7.81	ref 43
(1, 1, 0)	Hpydha$^-$	9.09	9.09	ref. 43
(1, 1, 0)	Hmemo$^+$	7.41	7.41	ref 44
(12, 4, 4)	$[\{V^VO_2(H_2bihyat)\}_4]^{4+}$	96.57 (7)		this work[c]
(2, 1, 1)	$[HV^VO_2(bihyat)]$	19.39 (6)	1.52	this work[c]
(1, 1, 1)	$[V^VO_2(bihyat)]^-$	17.87 (1)		this work[c]

[a] As the accurate pK_a value of Hbihyat$^-$ was not possible to be determined by potentiometry, this species was taken as component instead of bihyat^{2-} [b] $pH^+ + qH_2VO_4^- + rL^{k+} \rightleftharpoons [H_{p-2q}(VO_2)_q(L)_r]^{(rk+p-q)} + 2qH_2O$. [c] [$I$ = 0.20 M (KCl), 25 °C].

to vanadium(V) and becomes a stronger complexing agent only at pH values < 3.6.

Theoretical Study. The optimized molecular structures of the *cis*-$[V^VO_2(bihyat)]^-$ and $[V^V_2O_2(\mu_2\text{-}O)(bihyat)_2]$ at the B3LYP level are shown in Figure 8. Selected calculated and experimental bond lengths and angles are given in Supporting Information, Table S2. In the case of the dimer **3** the optimized structure differs substantially from the experimental one in terms of the relative orientation of the two $[V^VO(bihyat)]^+$ subunits. Thus, whereas the N(1)−V(1)···V(2)−N(7) dihedral angle in the X-ray structure is equal to 45° with a bend V(1)−O(4)−V(2) group (128.3°), the calculated structure is more expanded with the N(1)−V(1)···V(2)−N(7) angle being equal to 145° and an almost linear V(1)−O(4)−V(2) group (172.5°). This discrepancy was attributed to crystal packing effects. Nevertheless, an overall agreement has been found between the calculated and experimental geometrical parameters of the *cis*-$[V^VO_2(bihyat)]^-$ and those of the two $[V^VO(bihyat)]^+$ subunits for $[V^V_2O_3(bihyat)_2]$. The metal−ligand bond lengths are always longer than the experimental values particularly at the BP86 level, a fact that has been attributed to interatomic interactions present in solid state.[46,47]

The calculated frequencies at the B3LYP level of the stretching modes of the *cis*-$[V^VO_2]^+$ fragment of the anion *cis*-$[V^VO_2(bihyat)]^-$ are $\nu_s = 966$ cm^{-1} and $\nu_{as} = 986$ cm^{-1}. Thus, the experimental bands at 908 cm^{-1} and 922 cm^{-1} should be assigned to these metal centered vibrations. For the $[V^V_2O_3(bihyat)_2]$ complex the calculated frequencies are the asymmetric stretching vibration of the V−O−V group at 888 cm^{-1} and the ν(V=O) at 1034 cm^{-1} corresponding to the experimental bands at 856 cm^{-1} and 978 cm^{-1}. The most characteristic intraligand calculated and experimental frequencies, as well as the corresponding normal modes, are those shown in Figure 9. The high frequency but low intensity band at 1670−1690 cm^{-1} corresponding to the symmetric stretching of the two hydroxylamine groups is

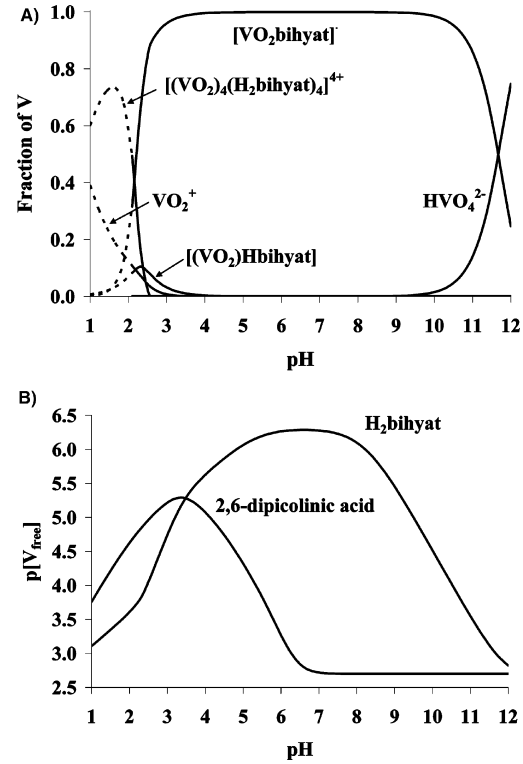


Figure 7. (A) Concentration distribution curves of vanadium(V) compounds formed in solutions of vanadium(V) and ligand H_2bihyat, with $C_V = 4.0 \times 10^{-3}$ M and L/M = 1, calculated by using the stability constants listed in Table 4. (B) Plot of p[V_{free}] versus pH under the same conditions for the vanadium(V)−H_2bihyat and vanadium(V)−H_2dipic systems. V_{free} means all the vanadium(V) species not containing H_2bihyat or 2,6-dipicolinic acid. Stability constants taken from ref 7a were performed at I = 0.40 M KCl.

(46) Snijders, J. G.; Baerends, E. J.; Vernooijs, P. *At. Data Nucl. Data Tables* **1982**, *26*, 483.
(47) (a) Snijders, J. G. *Mol. Phys.* **1978**, *36*, 1789. (b) Snijders, J. G.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909.

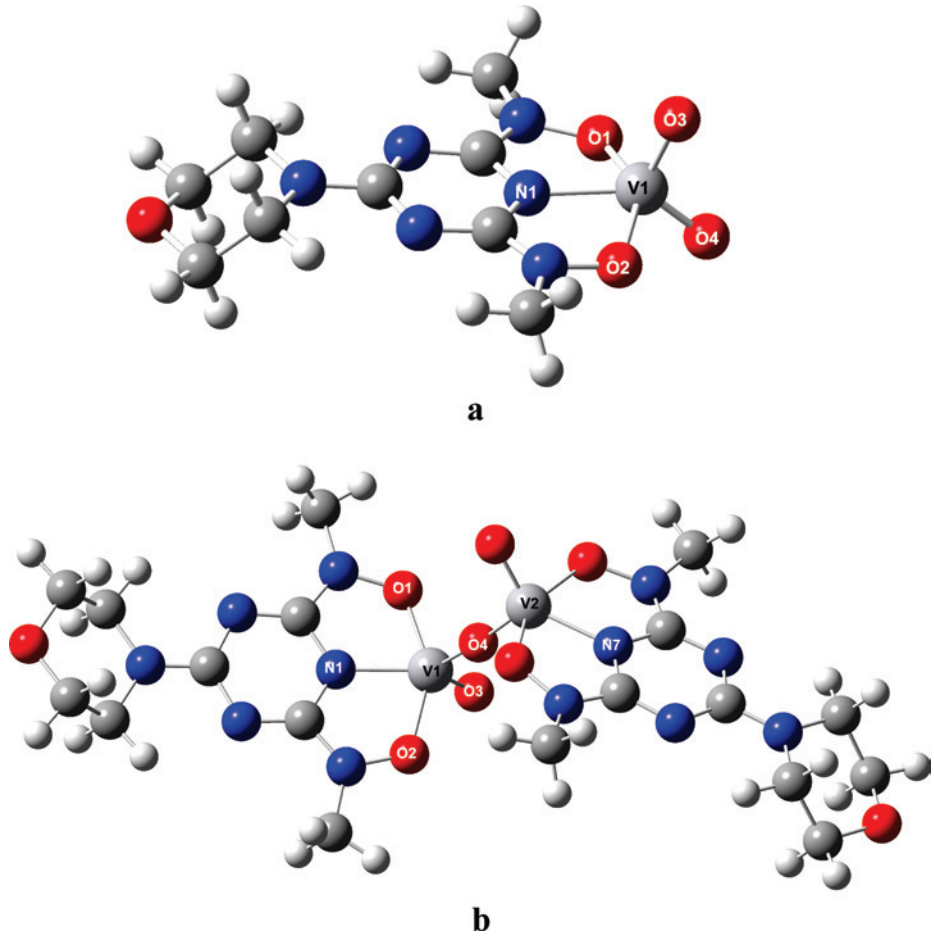
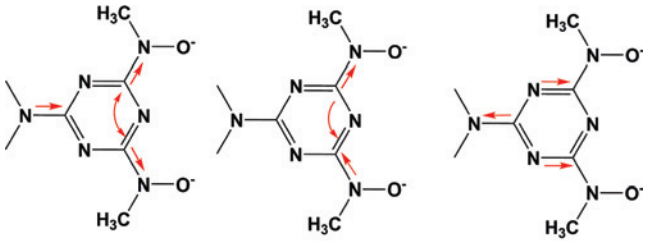


Figure 8. Optimized geometries of the compounds $Ph_4P[V^VO_2(bihyat)]$ (**a**) and $[V^V_2O_3(bihyat)_2]$ (**b**) at the B3LYP level.



H_2bihyat	1670 (23) -	1625 (560) *1562vs*	1571 (661)*1510vs*
cis-$[V^VO_2(bihyat)]$	1690 (113) *1648m*	1634 (617) *1580vs*	1549 (183)*1540vs*
$[V^V_2O_3(bihyat)_2]$	1684 (833) *1642s*	1555 (315)	1598 (3960) *1547vs*

Figure 9. Characteristic normal modes and calculated IR frequencies (cm^{-1}) at the B3LYP level. IR intensities ($KMmol^{-1}$) are given in parentheses. Experimental frequencies are given in italics.

not present in the experimental spectrum of the ligand. However, in the experimental spectra of complexes this band shifts by 20 cm^{-1} towards higher frequencies, gains intensity, and can be used as an indication of the tridentate coordination of the ligand. As the calculations have been carried out in the gas phase a discrepancy exists between the calculated and observed relative intensities.

The strength of the overall interaction between the metal fragment *cis*-$[V^VO_2]^+$ and the ligand dianion ($bihyat^{2-}$) has been studied with the EPA method of ADF,[35−37] where the bonding analysis was carried out by defining the ligand $bihyat^{2-}$ and the remaining metal fragment *cis*-$[V^VO_2]^+$ with the metal having a closed-shell configuration, as interacting species. The metal fragment−ligand dissociation energy, D_e, has been calculated equal to −429.4 and −387.1 kcal/mol, whereas the preparation energy equal to 34.2 and 30.1 at the B3LYP and BP86 levels, respectively. According to the EDA results the electrostatic interaction is −370.1 kcal/mol, accounting for the 67.6% of the total attractive interaction. The only stabilizing orbital interaction is this between the ligand occupied orbital with the d orbitals of the metal fragment, and no π-back bonding interaction is expected as the metals have a d^0 electronic configuration. This stabilizing interaction is equal to −177.5 kcal/mol and accounts for the 32.4% of the total attractive interaction. Finally, the repulsive Pauli interaction is equal to 130.4 kcal/mol.

The principal singlet-singlet electronic transitions, excitation energies, and oscillator strengths calculated by the TD-DFT methods at the B3LYP level are compiled in Table 5 along with the experimental data. The computed electronic transitions are in good agreement with the experimental ones. Compound **1** exhibits an intense band in the UV region of the spectra at about 300 nm being mainly an intraligand (LL) transition and a low intensity band at about 360 nm with a ligand-to-metal (LMCT) character. Concerning the dinuclear complex $[V^V_2O_3(bihyat)_2]$, the TD-DFT calculations have been carried out for both the optimized geometry, which is

Table 5. Principal Electronic Transitions, Wavelengths (λ), and Oscillator Strengths (f) Calculated at the B3LYP Level for the Vanadium(V) and Experimental Spectral UV/vis Data for Compounds **1** and **3**

	calculated			experimental	
	λ [nm]	f	assignment	solvent	λ_{max}, nm (ε, M^{-1} cm^{-1})
1	371	0.0000	LMCT π(L),p(O)→d	CH_2Cl_2	
	357	0.0002	LMCT π(L)→d		
	326	0.0014	LMCT π(L),p(O)→d		
	315	0.0011	LMCT p(O)→d		
	312	0.0292	LL π(L)→π^*(L)		300 (4470)
	305	0.0214	LMCT π(L)→d		
	295	0.0391	LL π(L),p(O)→π^*(L)		
	293	0.0022	LMCT π(L)→d		
	292	0.0055	LMCT π(L),p(O)→d		276 (13 840)
	283	0.0119	LMCT p(O)→d		269 (sh, 10 860)
					234 (59 910)
3[a]	644	0.1519	LMCT π(L),p(O)→d	CH_2Cl_2	637 (3500)
	623	0.0007	LMCT π(L),p(O)→d		
	590	0.0029	LMCT π(L)→d		
	588	0.0071	LMCT π(L),p(O)→d		
	423	0.0050	LMCT π(L),p(O)→d		
	408	0.0010	LMCT π(L),p(O)→d		
	400	0.0007	LMCT π(L),p(O)→d		401 (2900)
	400	0.0088	LMCT π(L),p(O)→d		
	391	0.0002	LMCT π(L),p(O)→d		
	386	0.0599	LMCT π(L),p(O)→d		
					275 (sh, 25 000)
					240 (65 130)
3[b]	673	0.0406	LMCT π(L),p(O)→d	Solid State	650
	621	0.0041	LMCT π(L),p(O)→d		
	576	0.0094	LMCT π(L),p(O)→d		
	576	0.0029	LMCT π(L),p(O)→d		
	447	0.0000	LMCT π(L),p(O)→d		
	421	0.0043	LMCT π(L),p(O)→d		420
	416	0.0006	LMCT π(L),p(O)→d		
	408	0.0000	LMCT π(L),p(O)→d		
	405	0.0004	LMCT π(L),p(O)→d		
	398	0.0187	LMCT π(L),p(O)→d		
					280(sh)
					254

[a] Optimized structure. [b] Structure determined by the X-ray structural analysis.

probably the adopted structure in solution, and the structure found in solid state by the X-ray study. Both calculations gave a similar pattern of bands. The MOs of the dimer in both geometries arise mainly from linear combinations of MOs of the monomer resulting in a lowering of the energy difference between the occupied and virtual orbitals. Thus, a strong red shift of absorption bands is predicted for the dimer (**3**) in comparison to the monomer (**1**) in agreement with the experiment. The dimer's (**3**) absorption bands arise from electronic transitions between highly delocalized π-MOs in the hydroxylamine ligand as well as the vanadyl oxygens and the low energy MOs located at the d-orbitals of the metals. These bands are centered at about 650, 580, 420, and 400 nm. To intuitively understand the absorption processes, representative density diagrams of the MOs involved in each principal electronic transition for the studied compounds are depicted in Supporting Information, Figures S1, S2, and S3. The configuration interaction (CI) coefficients giving the weight of the participation of each single MO excitation to the overall transition are also given.

Conclusions

We have synthesized and structurally characterized the vanadium(V) compounds $[V^{V}_2O_2(\mu_2\text{-}O)(bihyat)_2]$ and $Ph_4P[V^{V}O_2(bihyat)]$. Both compounds represent the first vanadium complexes with bis-(hydroxyamino)-1,3,5-triazine-type ligands, which constitute a class of complexing agents for metal ions in their highest oxidation states. The results of density functional calculations showed that the attractive metal−ligand interaction is due to electrostatic (67.6 %) and orbital interactions (32.4 %) and was used to analyze the vibration spectra of the compounds. Finally, the TD-DFT calculated principal singlet-singlet electronic transitions were used for the assignment of the bands in the electronic spectra of the complexes. From multinuclear NMR measurements in aqueous solution of the anion *cis*-$[V^{V}O_2(bihyat)]^-$ of the compound $C(NH_2)_3[V^{V}O_2(bihyat)]$, it is clear that this species is not only air stable, but it is also highly resistant towards hydrolysis in a wide pH range, 3.3−11.0. The 2D $\{^1H\}$ EXSY spectrum of *cis*-$[V^{V}O_2(bihyat)]^-$ proved that this species is more kinetically inert than its dipicolinate analogue. Potentiometry supported the conclusions drawn from the NMR measurements giving a stability constant for *cis*-$[V^{V}O_2(bihyat)]^-$ of 10^{18}. Thus, the high affinity of H_2bihyat for $V^{V}O_2^+$ species, its tridentate character, as well as its small size, opens the door for widely different applications in medicine, analysis, and catalysis for *cis*-$[V^{V}O_2(bihyat)]^-$ and vanadium(V)-bis-(hydroxyamino)-triazine compounds in general. The investigation of insulinomimetic and anticancer

activity of $(CH_6N_3)[V^VO_2(bihyat)]$ is currently being carried out in cooperation with other laboratories.

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Supporting Information Available: Further details are given in Figures S1−S3, Scheme S1, and Tables S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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