Inorg. Chem. **2007**, *46*, 5069–5075

Inorganic Chemistry
Article

Simple General Method of Generating Non-oxo, Non-amavadine Model Octacoordinated Vanadium(IV) Complexes of Some Tetradentate ONNO Chelating Ligands from Various Oxovanadium(IV/V) Compounds and Structural Characterization of One of Them

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Received November 24, 2006

A simple general route of obtaining very stable octacoordinated non-oxovanadium(IV) complexes of the general formula VL_2 (where H_2L is a tetradentate ONNO donor) is presented. Six such complexes (**1**–**6**) are adequately characterized by elemental analysis, mass spectrometry, and various spectroscopic techniques. One of these compounds (**1**) has been structurally characterized. The molecule has crystallographic $\bar{4}$ symmetry and has a dodecahedral structure existing in a tetragonal space group $P\bar{4}n2$. The non-oxo character and VL_2 stoichiometry for all of the complexes are established from analytical and mass spectrometric data. In addition, the non-oxo character is clearly indicated by the complete absence of the strong $\nu_{V=O}$ band in the 925–1025 cm^{-1} region, which is a signature of all oxovanadium species. The complexes are quite stable in open air in the solid state and in solution, a phenomenon rarely observed in non-oxovanadium(IV) or bare vanadium(IV) complexes.

Introduction

Though octacoordination is not frequently met in the domain of coordination chemistry of the first-row transition elements, the octacoordinated vanadium(IV) complex amavadine was isolated from Amanita mushrooms way back in the early 1970s.[1,2] It was originally thought to be an oxovanadium complex, but later on it was established that it contains a "non-oxo" or "bare" V^{4+} center.[3,4] The structure of amavadine having a N_2O_6 donor environment and its non-oxovanadium(IV) character was also established by its total synthesis.[5] Several synthetic models of amavadine were subsequently prepared and structurally characterized.[4−9] Some of these model complexes were examined for their peroxidase activity in terms of the catalytic oxidation of some selected thiols to the corresponding disulfides and also for their peroxydative halogenation and catalase activity in terms of decomposition of H_2O_2.[10−12] The role of such model complexes in the hydroxylation or oxofunctionalization of alkanes and some selected aromatic compounds at room

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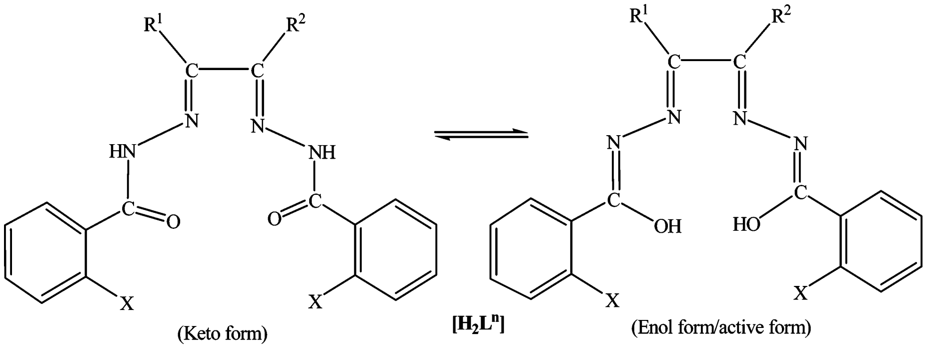

Figure 1. 2D line drawing of the ligands. In H_2L^1, $R^1 = R^2 = C_6H_5$ and X = NH_2; in H_2L^2, $R^1 = R^2 = C_6H_5$ and X = OH; in H_2L^3, $R^1 = R^2 = C_6H_5$ and X = H; in H_2L^4, $R^1 = CH_3$, $R^2 = C_2H_5$, and X = NH_2; in H_2L^5, $R^1 = CH_3$, $R^2 = C_2H_5$, and X = OH; in H_2L^6, $R^1 = CH_3$, $R^2 = C_2H_5$, and X = H.

temperature was also explored.[12] A survey of older as well as recent literature revealed that some sulfur-coordinated[13] and a few peroxo-ligated octacoordinated bare vanadium(IV) complexes[14] were known, but apart from synthetic analogues of amavadine, no reports of other types of octacoordinated non-oxovanadium(IV) complexes with multidentate N−O donor ligands have appeared. Such a void has probably been created as a result of overfocusing on modeling of the naturally occurring amavadine expected to mimic that biomolecule. In this work, we report the synthesis of several octacoordinated non-amavadine model complexes of some selected dianionic tetradentate N−O donor ligands. These complexes are fully characterized by various physicochemical techniques.

Experimental Section

Materials. $[VO(acac)_2]$ was prepared as described in the literature.[15] Other vanadium compounds used in this work, $[VO(DPA)(H_2O)_2]$,[16] [VO(DPA)(*o*-phen)],[17] $[V(PA)_3]\cdot 3H_2O$,[18] [VO(OEt)L], [VO(OMe)L], and [VO(OEt)L(py)],[19] were also obtained by previously reported procedures. VCl_3 was purchased from Fluka. Reagent-grade solvents were dried and distilled prior to use. All other chemicals were reagent-grade, were obtained from commercial sources, and were used without further purification. Spectroscopic-grade solvents were used for spectral measurements.

Synthesis. Syntheses of the Ligands H_2L^1−H_2L^6. The Schiff base ligands benzildihydrazone of 2-aminobenzoylhydrazine (**H_2L^1**), benzildihydrazone of 2-hydroxybenzoylhydrazine (**H_2L^2**), benzildihydrazone of benzoylhydrazine (**H_2L^3**), pentane-2,3-dihydrazone of 2-aminobenzoylhydrazine (**H_2L^4**), pentane-2,3-dihydrazone of 2-hydroxybenzoylhydrazine (**H_2L^5**), and pentane-2,3-dihydrazone of benzoylhydrazine (**H_2L^6**) were prepared by a previously reported procedure.[20] Elemental analysis results, melting points, and NMR and IR data for all of these were also verified and reported below (Figure 1).

H_2L^1. Yield: 70%. Mp: 226 °C. Anal. Calcd for $C_{28}H_{24}N_6O_2$: C, 70.59; H, 5.04; N, 17.65. Found: C, 70.54; H, 5.02; N, 17.66. IR (KBr, cm^{-1}): 3462 ($\nu(NH_2)_s$), 3355 ($\nu(NH_2)_{as}$), 3027 (ν(NH)), 1661 (ν(C=O)), 1500 (ν(C=N)), 1241 (ν(N−N)). ^1H NMR (DMSO-d_6, δ): 7.90 (s, 2H, −CH=N), 7.48−6.51 (m, 18H, C_6H_5, C_6H_4), 5.5 (s, 4H, NH_2).

H_2L^2. Yield: 74%. Mp: 208 °C (dec). Anal. Calcd for $C_{28}H_{22}N_4O_4$: C, 70.29; H, 4.60; N, 11.71. Found: C, 70.26; H, 4.54; N, 11.66. IR (KBr, cm^{-1}): 3284 (ν(OH)), 3029 (ν(NH)), 1636 (ν(C=O)), 1532 (ν(C=N)), 1232 (ν(N−N)). ^1H NMR (DMSO-d_6, δ): 11.74 (s, 2H, OH), 7.97 (s, 2H, −CH=N), 7.69−6.84 (m, 18H, C_6H_5, C_6H_4).

H_2L^3. Yield: 70%. Mp: 210 °C. Anal. Calcd for $C_{28}H_{22}N_4O_2$: C, 75.34; H, 4.93; N, 12.56. Found: C, 75.29; H, 4.88; N, 12.54. IR (KBr, cm^{-1}): 3175 (ν(NH)), 1646 (ν(C=O)), 1526 (ν(C=N)), 1261 (ν(N−N)). ^1H NMR (DMSO-d_6, δ): 7.91 (s, 2H, −CH=N), 7.61−6.82 (m, 20H, C_6H_5).

H_2L^4. Yield: 70%. Mp: 224 °C. Anal. Calcd for $C_{19}H_{22}N_6O_2$: C, 62.29; H, 6.01; N, 22.95. Found: C, 62.27; H, 5.96; N, 22.92. IR (KBr; cm^{-1}): 3471 ($\nu(NH_2)_s$), 3363 ($\nu(NH_2)_{as}$), 3219 (ν(NH)), 1644 (ν(C=O)), 1522 (ν(C=N)), 1252 (ν(N−N)). ^1H NMR (DMSO-d_6, δ): 7.90 (s, 2H, −CH=N), 7.56−6.75 (m, 8H, C_6H_4), 6.12 (s, 4H, NH_2), 2.20 (s, 3H, CH_3), 2.51 (q, 2H, CH_2, Et, J = 6.8 Hz), 1.08 (t, 3H, CH_3, Et, J = 7.1 Hz).

H_2L^5. Yield: 70%. Mp: 238 °C. Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 51.63; H, 5.43; N, 15.22. Found: C, 51.59, H, 5.38; N, 15.26. IR (KBr, cm^{-1}): 3053 (ν(OH)), 3268 (ν(NH)), 1642 (ν(C=O)), 1537 (ν(C=N)), 1226 (ν(N−N)). ^1H NMR (DMSO-d_6, δ): 11.80 (s, 2H, OH), 8.01 (s, 2H, −CH=N), 7.46−6.98 (m, 8H, C_6H_4), 2.25 (s, 3H, CH_3), 2.51 (q, 2H, CH_2, Et, J = 7.0 Hz), 1.12 (t, 3H, CH_3, Et, J = 7.1 Hz).

H_2L^6. Yield: 70%. Mp: 242 °C. Anal. Calcd for $C_{19}H_{20}N_4O_2$: C, 67.86; H, 5.95; N, 16.67. Found: C, 67.84; H, 5.91; N, 16.69. IR (KBr, cm^{-1}): 3171 (ν(NH)), 1659 (ν(C=O)), 1531 (ν(C=N)), 1278 (ν(N−N)). ^1H NMR (DMSO-d_6, δ): 7.81 (s, 2H, −CH=N),

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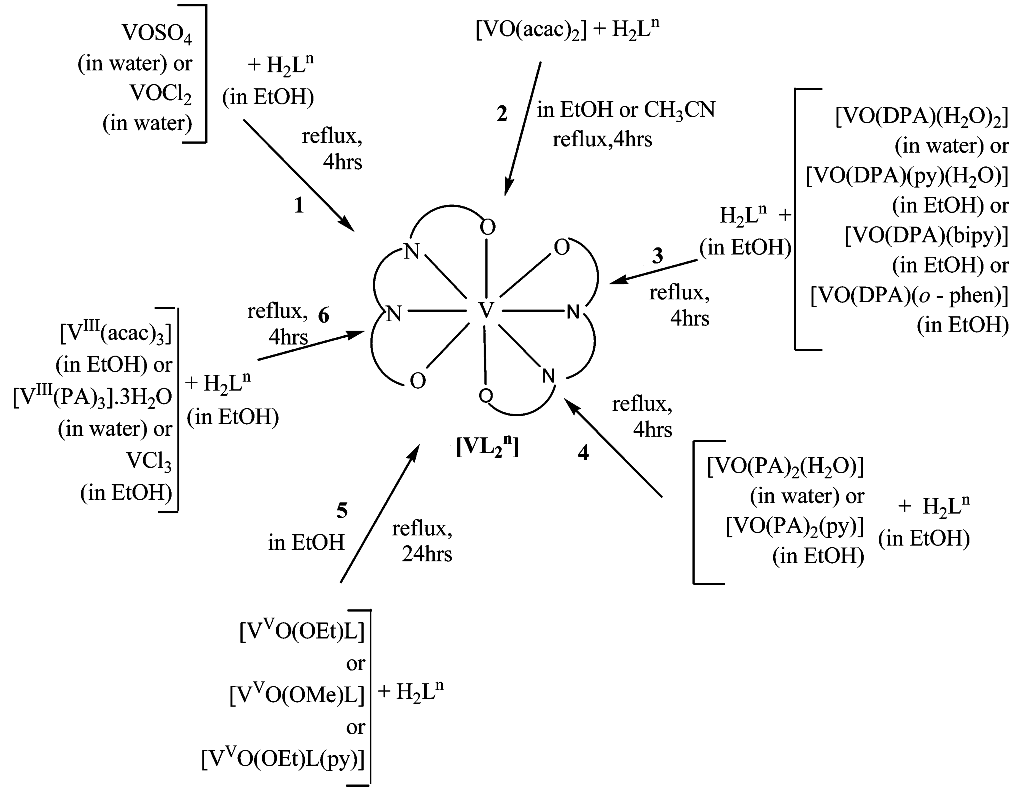
Scheme 1 [a]



[a] In all preparative procedures, the vanadium-containing starting material/ligand ratio taken is 1:2. $\mathbf{H_2L}^n = \mathbf{H_2L}^{1-6}$. $DPAH_2$ = pyridine-2,6-dicarboxylic acid; PAH = pyridine-2-carboxylic acid; VO(OEt)L = oxoethoxovanadium(V) complex of 2-hydroxybenzoylhydrazone of 2-hydroxybenzoylhydrazine.

7.58−6.86 (m, 10H, C_6H_5), 2.21 (s, 3H, CH_3), 2.50 (q, 2H, CH_2, Et, J = 6.9 Hz), 1.01 (t, 3H, CH_3, Et, J = 7.1 Hz).

Synthesis of Octacoordinated Non-oxovanadium(IV) Complexes. All of the six complexes were synthesized by a simple general method using various oxovanadium(IV), oxovanadium(V), and vanadium(III) compounds as starting materials mentioned in the Materials section and in Scheme 1.

V(L^1)$_2$ (1). A total of 0.476 g (1.0 mmol) of $\mathbf{H_2L^1}$ was dissolved in 30 mL of ethanol or acetonitrile, and 0.135 g (0.5 mmol) of $VO(acac)_2$ was added to the ligand solution. The mixture was then refluxed for 4 h on a steam bath. The color of the solution slowly changed from dark brown to reddish brown, and a reddish-brown solid separated out. The solution was filtered, and the reddish-brown residue was collected. The compound was recrystallized from a mixture of dichloromethane−ethanol. After 2 weeks, reddish-brown single crystals separated out from the solution that were suitable for X-ray diffraction analysis. Yield: 68%. Anal. Calcd for $C_{56}H_{44}N_{12}O_4V$: C, 67.27; H, 4.40; N, 16.82; V, 5.10. Found: C, 67.25; H, 4.34; N, 16.84; V, 5.09. λ_{max}, nm (ϵ, L M^{-1} cm^{-1}) (CH_3CN): 566 (10 420), 480 (18 996), 298 (49 325). IR (KBr, cm^{-1}): 3458 ($\nu(NH_2)_s$), 3361 ($\nu(NH_2)_{as}$), 1501 (ν(C═N)), 1243 (ν(N−N)), 1084 (ν(C−O/enolic)). ESMS (%): m/z 999 (100) [M^+].

V(L^2)$_2$ (2). The compound was obtained by the same method as that of the reddish-brown solid. Yield: 64%. Anal. Calcd for $C_{56}H_{40}N_8O_8V$: C, 67.00; H, 3.99; N, 11.16; V, 5.08. Found: C, 66.96; H, 3.91; N, 11.13; V, 5.06. λ_{max}, nm (ϵ, L M^{-1} cm^{-1}) (CH_3CN): 557 (4019), 452 (13 882), 287 (30 663), 273 (31 080). IR (KBr, cm^{-1}): 3254 (ν(OH)), 1535 (ν(C═N)), 1239 (ν(N−N)), 1096 (ν(C−O/enolic)). ESMS (%): m/z 1003 (100) [M^+].

V(L^3)$_2$ (3). The compound was obtained by the same method as that of the reddish-brown solid. Yield: 68%. Anal. Calcd for $C_{56}H_{40}N_8O_4V$: C, 71.56; H, 4.26; N, 11.93; V, 5.43. Found: C, 71.52; H, 4.22; N, 11.96; V, 5.40. λ_{max}, nm (ϵ, L M^{-1} cm^{-1}) (CH_3CN): 546 (5470), 440 (13 226), 302 (42 936), 280 (42 661). IR (KBr, cm^{-1}): 1532 (ν(C═N)), 1265 (ν(N−N)), 1076 (ν(C−O/enolic)). ESMS (%): m/z 939 (100) [M^+].

V(L^4)$_2$ (4). The compound was obtained by the same method as that of the reddish-brown solid. Yield: 69%. Anal. Calcd for $C_{38}H_{40}N_{12}O_4V$: C, 58.54; H, 5.13; N, 21.57; V, 6.55. Found: C, 58.51; H, 5.09; N, 21.55; V, 6.52. λ_{max}, nm (ϵ, L M^{-1} cm^{-1}) (CH_3CN): 556 (5057), 431 (13 827), 282 (23 365). IR (KBr, cm^{-1}): 3429 ($\nu(NH_2)_s$), 3342 ($\nu(NH_2)_{as}$), 1519 (ν(C═N)), 1257 (ν(N−N)), 1052 (ν(C−O/enolic)). ESMS (%): m/z 779 (100) [M^+].

V(L^5)$_2$ (5). The compound was obtained by the same method as that of the reddish-brown solid. Yield: 72%. Anal. Calcd for $C_{38}H_{36}N_8O_8V$: C, 58.24; H, 4.60; N, 14.30; V, 6.51. Found: C, 58.22; H, 4.47; N, 14.27; V, 6.48. λ_{max}, nm (ϵ, L M^{-1} cm^{-1}) (CH_3CN): 542 (4035), 429 (14 785), 284 (22 525), 273 (22 761). IR (KBr, cm^{-1}): 3238 (ν(OH)), 1592 (ν(C═N)), 1208 (ν(N−N)), 1042 (ν(C−O/enolic)). ESMS (%): m/z 783 (100) [M^+].

V(L^6)$_2$ (6). The compound was obtained by the same method as that of the reddish-brown solid. Yield: 68%. Anal. Calcd for $C_{38}H_{36}N_8O_4V$: C, 63.42; H, 5.01; N, 15.58; V, 7.09. Found: C, 63.38; H, 4.95; N, 15.56; V, 7.04. λ_{max}, nm (ϵ, L M^{-1} cm^{-1}) (CH_3CN): 544 (3714), 427 (10 124), 280 (25 198), 263 (25 272). IR (KBr, cm^{-1}): 1551 (ν(C═N)), 1204 (ν(N−N)), 1060 (ν(C−O/enolic)). ESMS (%): m/z 719 (100) [M^+].

Physical Measurements. Elemental analyses (C, H, and N) were done with a Perkin-Elmer 2400 CHNS/O analyzer, and vanadium contents (%) of the complexes were determined gravimetrically as V_2O_5.[16] Melting points were determined in an electrically controlled melting point apparatus (Sunvic, Glasgow, U.K.). Electronic spectra of the complexes in acetonitrile were recorded on a Hitachi U-3501 spectrophotometer, and IR spectra (as KBr pellets) were taken with a Perkin-Elmer RXI Fourier transform IR spectrophotometer. The ^1H NMR spectra were recorded on a Bruker model Advance DPX300 spectrometer. The mass spectra were taken with a Micromass LCT electrospray mass spectrometer equipped an electrospray ionization system. Electron paramagnetic resonance (EPR) spectra were obtained at X-band frequencies on a Varian E-109C spectrometer around 110 K. The experiments were carried out using a Varian variable-temperature accessory. This accessory utilizes an open gas-flow system and uses liquid nitrogen as a coolant. Nitrogen gas is used to cool the sample. The calibrant was tetracyanoethylene ($g = 2.002\ 77$). Electrochemical measurements were performed with a PAR model 362 scanning potentiostat, and cyclic voltammograms were recorded at 25 °C in the designated solvents under dry dintrogen with the electroactive component at ca. 10^{-3} M. Tetraethylammonium perchlorate (NEt_4ClO_4; 0.1 M) was used as the supporting electrolyte. A three-electrode configuration was employed with a platinum working electrode, a calomel reference electrode, and a platinum auxiliary electrode. The ferrocene/ferrocenium (Fc/Fc^+) couple was used as the internal standard.[21] Thermal analysis was carried out on a Mettler-Toledo TGA/DTA 851 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate: 30 $cm^3\ min^{-1}$). The samples were heated in an alumina crucible at a rate of 10 °C min^{-1}. Room-temperature magnetic susceptibilities of complexes were measured in the polycrystalline state on a PAR 155 sample vibrating magnetometer using $Hg[Co(SCN)_4]$ as the calibrant.

Results and Discussion

The most remarkable feature of the present study is the general nature of the synthetic procedures. Here condensations of different α−α diketones and different ring-substituted aromatic acid hydrazides are found to lead to a series of diprotic tetradentate ONNO chelating ligands, all of which are capable of forming octacoordinated non-oxovanadium(IV) complexes from various oxovanadium(IV) and -(V) compounds. Such ligands acting in the dianionic form are found to be capable of oxo abstraction from the starting oxovanadium(IV) species as well as stabilization of the “bare” V^{4+} center. The use of acid hydrazides as the amine fragment appears to be essential for oxo abstraction because diamine-based similar ligands like “salen” afforded hexacoordinated oxovanadium(IV) complexes and not the octacoordinated non-oxovanadium(IV) complexes.[22a−h] The same octacoordinated non-oxovanadium(IV) complexes are also obtained from some vanadium(III) compounds (Scheme 1, reaction 6). Because the reactions are done in open air, vanadium(III) is oxidized to VO^{2+}, which is then deoxygenated by the ligand. It is observed in the present case that even if a 1:1 metal-to-ligand ratio is used during preparation, the 1:2 complex is formed and the 1:1 complex could never be isolated. Such an observation was reported previously in the case of some synthetic amavadine models.[23]

Utilization of simple and complex oxovanadium(IV) species as starting materials leading to the formation of non-oxovanadium(IV) complexes depends mainly on the choice of an appropriate ligand, which is able to donate enough electron density (σ and π) to the central metal ion to neutralize its +ve charge and stabilize the bare non-oxo acceptor center.[24] The formation of hexacoordinated non-oxovanadium(IV) species is very much sensitive to experimental conditions because of the combination of acid−base and redox reactions in such systems.[25] In this case, the hard acceptor character of V^{4+} favors coordination from the hard donor points N and O. Studies on hexacoordinated non-oxovanadium(IV) complexes indicated that not only are the proper choice of the reaction conditions essential but scrupulous maintenance of those conditions is also vitally important for the successful synthesis of such complexes.[26] It is noteworthy that no such stringent conditions are required in the present case. The reactions can be performed in ordinary ethanol (containing 1−3% water) and under open atmospheric conditions. It does not require a dry solvent, the presence of a baselike Et_3N, or an inert atmosphere, which were thought by previous workers to be essential.[24,26] However, it is to be noted that these are general advantages over the previous method used for generating a non-oxovanadium center (existing in a hexacoordinated environment) from the corresponding oxovanadium species and may not be viewed as particularly relevant to the methods of preparing amavadine models. The compounds are quite stable in the open air in the solid state and in solution, which is rather uncommon for “bare” vanadium(IV) or non-oxovanadium(IV) complexes. Stability of the complexes may be due to the simultaneous oxo removal and complete charge neutralization as well as the formation of eight strong covalent bonds at the V^{4+} center, which possibly precludes the approach of a reagent species within the reaction sphere of the well-protected V^{4+} center. Also, the rigidity and steric bulk of the ligands do not permit the formation of the square-pyramidal pentacoordinated VOL complex so familiar in vanadium chemistry, in which the terminal oxygen is in an axial position and the tetradentate ligand occupies the equatorial plane. The overall neutral/ uncharged state of all of the complexes (**1**−**6**) is revealed by their high solubility in solvents like benzene, toluene, dichloromethane, and chloroform.

Scheme 1 presents the various pathways through which the octacoordinated non-oxo VL_2 type of vanadium(IV) complex can be obtained. It reveals that the octacoordinated non-oxovanadium(IV) complexes can be obtained by the

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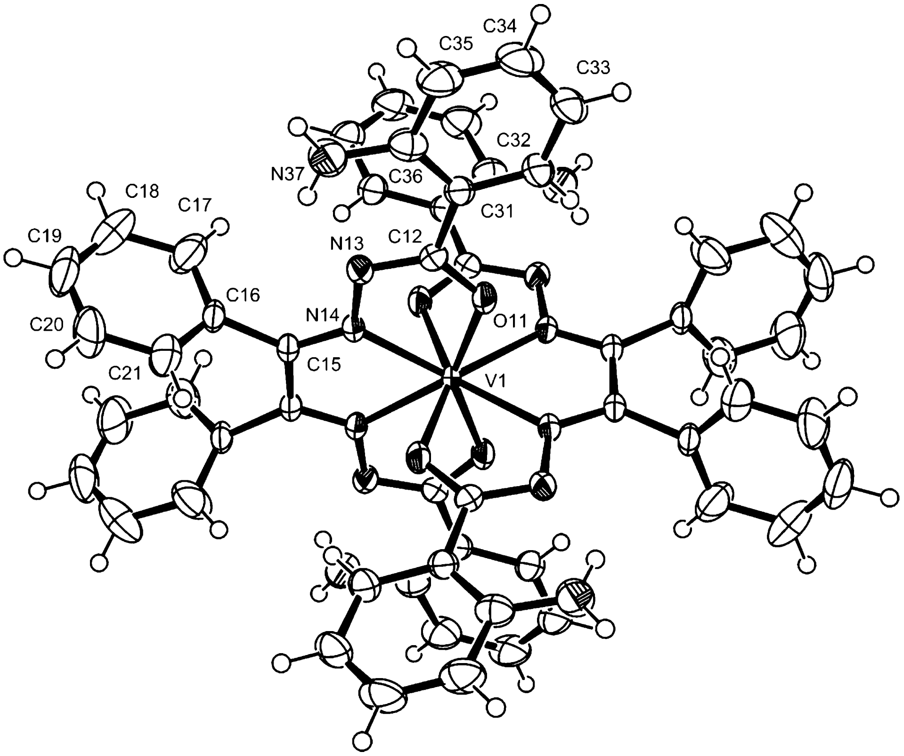

Figure 2. Structure of **1** showing the atomic numbering scheme with ellipsoids at 50% probability. The molecule has crystallographic $\bar{4}$ symmetry.

reaction of the LH_2-type ligands used in this work with a large number of oxovanadium(IV) compounds, simple (reaction 1) or complex (reactions 2−4). The formation of $V^{IV}L_2$ complexes from oxovanadium(V) species is shown by reaction 5, which probably involved a step of reduction from vanadium(V) to vanadium(IV) followed by oxo abstraction from the oxovanadium(IV) species generated in situ. Reaction 6 illustrates the formation of $V^{IV}L_2$ complexes from three vanadium(III) compounds. Here, the vanadium(III) species is oxidized by oxygen of air because the reaction is performed in the open air.

Crystal Structure Data Collection. Data were measured with Mo Kα radiation using a Marresearch image plate system. Data analysis was carried out with the *XDS* program[27] to provide 2343 independent reflections. The structure was solved using direct methods with the *SHELX-97* program.[28a] Non-H atoms were refined with anisotropic thermal parameters. The H atoms bonded to C were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was refined on F^2 using the *SHELX-97* program. Maximum and minimum residual electron densities were $+0.179$ and -0.169 e Å^{-3}.

Description of the Crystal Structure. The structure of **1** is shown in Figure 2. The metal atom sits on a $\bar{4}$ site; therefore, the coordination environment is a dodecahedron. The two independent distances are V−O = 2.038(2) Å and V−N = 2.152(3) Å. In order to assess these bond lengths, we searched the Cambridge Crystallographic Database[28b] for hexacoordinated vanadium(IV) complexes containing at least one O and one N coordinated atom but with no terminal O atoms. The average bond lengths for 38 examples were V−O = 1.866 Å and V−N = 2.146 Å. Thus, in the present structure, the V−O bond is slightly longer than this average, but the V−N bond length is very similar. There are no examples of octacoordinated vanadium(IV) complexes in the database apart from three that contained hydroxyimino groups forming V−N−O three-membered rings.[6,8] This clearly demonstrates both the uniqueness of the present structure and the fact that the bonds in the present octacoordinated complex are particularly strong. The free $-NH_2$ group in the ligand, N37, is involved in two hydrogen bonds via its two H atoms. It forms an intramolecular hydrogen bond to N13 with dimensions N37−H···N13: N···N = 2.743(4) Å, H···N = 2.12 Å, and N−H···N = 129°.

IR and ^{1}H NMR Spectroscopy. The IR data of all of the six ligands (**H_2L^{1-6}**) and their complexes (**1**−**6**) are presented in the Experimental Section. The presence of a free $-NH_2$ group in ligands **H_2L^1**, **H_2L^4**, and their corresponding complexes **1** and **4** is shown by the occurrence of symmetric and antisymmetric modes of the $\nu(NH_2)$ band within the ranges of 3471−3429 and 3363−3342 cm^{-1} and clearly indicates that the ring $-NH_2$ group[29] does not participate in coordination to the central metal ion. The disappearance of the ν_{NH} and $\nu_{C=O}$ bands of the ligand in the metal complexes and the appearance of a new band in the 1013−1084 cm^{-1} range due to $\nu_{C-O(enolate)}$ clearly demonstrate that complex formation takes place via enolization of the ligand. Some

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Table 1. Crystal Data and Structure Determination Summary of Complex **1**

empirical formula	$C_{56}H_{44}N_{12}O_4V$
fw	999.97
cryst syst	tetragonal
space group	$P\bar{4}n2$ (No. 118)
a (Å)	11.438(12)
c (Å)	18.720(19)
V (Å^3)	2449(4)
Z	2
D_{calc} (g cm^{-3})	1.356
data/restraints/param	2343/0/167
no. of obsd reflns [$I > 2\sigma(I)$]	2241
R1, wR2 (obsd data)[a]	0.0383, 0.0930
R1, wR2 (all data)[a]	0.0404, 0.0942
R_{int}	0.044
peaks in the final difference map (e A^{-3})	0.18, −0.17
GOF on F^2	1.062

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$.

Table 2. Molecular Dimensions in Complex **1** (Distances, Å; Angles, deg)[a]

Bond Distance			
V1−O11	2.038(3)	V1−N14	2.153(3)
Bond Angle			
O11−V1−O11($1)	97.43(7)	O11−V1−N14($3)	142.20(7)
O11−V1−O11)($2)	92.00(6)	O11−V1−N14($2)	75.43(7)
O11−V1−O11($3)	146.69(6)	N14−V1−N14($1)	131.82(7)
O11−V1−N14($1)	77.60(7)	N14−V1−N14($2)	131.06(7)
O11−V1−N14	71.10(7)	N14−V1−N14($3)	71.11(7)

[a] Symmetry elements: $1, 1 − *x*, −*y*, *z*; $2, 0.5 + *y*, *x* − 0.5, 0.5 − *z*; $3, 0.5 − *y*, 0.5 − *x*, 0.5 − *z*.

other characteristic bands are given in the Experimental Section. A remarkable feature of the IR spectra of all of the metal complexes is the complete absence of the $\nu_{V=O}$ band in the 935−1035 cm^{-1} region.[30] Thus, all of the vanadium(IV) complexes (**1**−**6**) are non-oxo in nature, and this conclusion is supported by the mass spectra, elemental analysis data for the complexes (**2**−**5**), and X-ray crystallographic analysis (of compound **1**; see Tables 1 and 2). ^{1}H NMR data of all of the six ligands ($\mathbf{H_2L^{1-6}}$) are given in the Experimental Section.

Mass Spectra. Mass spectral data of all of the complexes, along with their molecular weights calculated on the basis of their formula VL_2, are presented in Experimental Section. The 100% peak at *m/z* 999 corresponds to the molecular ion of the structurally characterized complex **1** and is exactly equal to its molecular weight calculated on the basis of the formula $V(L^1)_2$ containing the non-oxovanadium(IV) center. The absence of other peaks of significance (i.e., peaks of intensity >10%) in the mass spectra of other complexes (**2**−**6**) reveals that all of the four donor (O^-NNO^-) points of each of the two tetradentate chelating ligands are attached firmly to the V^{4+} acceptor center. This is corroborated by thermal studies of these $V^{IV}L_2$ complexes in air, which are found to remain stable up to ∼300 °C. Thus, the 1:2 metal-to-ligand stoichiometry, non-oxo character, and octacoordinated nature of all of these vanadium(IV) complexes are established from the mass spectrometric study, which is confirmed by the X-ray structural study of complex **1**.

Electronic Spectra. Electronic spectra of complexes **1**−**6** were recorded in both noncoordinating (CH_2Cl_2) and coordinating (DMF and DMSO) solvents as well as in the solid state in the 200−1200 nm range. Spectral data collected in a CH_2Cl_2 solution are given in the Experimental Section. Spectra of all of the complexes exhibit primarily two high-intensity transitions: one in the 550−580 nm range and another in the 430−480 nm region. By analogy to previously reported non-oxovanadium(IV) complexes,[24,26] both of these bands are assigned to enolate−O → vanadium(IV) charge-transfer transitions. The same features were observed when spectra of the compounds were recorded in coordinating solvents like DMF and DMSO. Also, no change in the spectral features is noted when spectra of the solid compounds were recorded in the reflectance mode. These observations imply that the same complex species is present under all of the above conditions and points to their high stability. All of the other high-energy bands lying below 350 nm are due to intraligand transitions.

Magnetic Moment and EPR Spectra. Room-temperature (25 °C) magnetic moments of complexes **1**−**6** lie around 1.7 μ_B (Table 3), which is consistent with the spin-only moment of monomeric vanadium(IV) complexes. X-band spectra of all of the complexes were recorded in a CH_2Cl_2 solution at room temperature and as a frozen glass at liquid nitrogen temperature and are presented in Table 3. All of the spectra exhibit eight line patterns typical of vanadium(IV) (^{51}V; $I = {}^7/_2$) at room temperature and the usual hyperfine splitting at low temperature. As the charge on the ion increases, covalent character becomes progressively important in the case of the system with a d^1 configuration. As a result, the effective value of the spin−orbit coupling parameter is lowered and in some cases may reverse the expected relative magnitudes of the *g* components. EPR parameters, which are less than g_e for all of the complexes, indicate that the V^{4+} center is in the $(d_{x^2-y^2})^1$ configuration. In the structure of complex **1**, all of the chelate rings are five-membered, where two donor atoms of the same type are trans to each other (along the axial direction). The structure of **1** clearly shows that the coordination environment around the bare V^{4+} center is dodecahedral and for dodecahedral complexes with a d^1 configuration of the central metal ion $g_\perp > g_\parallel$,[13b] as is observed in the present case.

Electrochemistry. Cyclic voltammetric data for complexes **1**−**6** are presented in Table 3. All of the complexes (**1**−**6**) seem to display an electrochemical irreversible (but chemical reversible) one-step one-electron response in the 1.14−1.18 V range corresponding to vanadium(IV)/vanadium(V) oxidation.[19,31] This is substantiated by the following facts. In the voltage range used in this work (0.6−1.6 V), the ligand itself and their zinc complexes do not exhibit any oxidative response. Hence, the free ligand or its coordinated form does not undergo oxidation in the operative voltage range.

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Table 3. Magnetic Moment, EPR,[a] and Cyclic Voltammetric Data for Complexes **1**−**6**

	rt			~110 K				
compound	μ_{eff}[b] (μ_B)	g_{av}	A_{av} (10^{-4} cm^{-1})	$g_{\parallel}$	$A_{\parallel}$ (10^{-4} cm^{-1})	$g_{\perp}$[c]	$A_{\perp}$[d] (10^{-4} cm^{-1})	$E_{1/2}$[e] (V) [ΔE_p[f] (mV)]
$V(L^1)_2$ (**1**)	1.71	1.954	69.3	1.937	139	1.962	34.4	+1.18 [130]
$V(L^2)_2$ (**2**)	1.72	1.956	69.3	1.945	137	1.961	35.4	+1.17 [171]
$V(L^3)_2$ (**3**)	1.69	1.956	69.3	1.953	136	1.957	35.9	+1.14 [147]
$V(L^4)_2$ (**4**)	1.68	1.957	70.5	1.942	138	1.964	36.7	+1.17 [135]
$V(L^5)_2$ (**5**)	1.70	1.957	70.7	1.945	140	1.963	36.0	+1.15 [132]
$V(L^6)_2$ (**6**)	1.69	1.956	70.5	1.943	137	1.962	37.2	+1.18 [156]

[a] In dichloromethane (at room temperature and ~110 K). [b] In the solid state. [c] $g_{\mathrm{av}} = (g_{\parallel} + 2g_{\perp})/3$. [d] $A_{\mathrm{av}} = (A_{\parallel} + 2A_{\perp})/3$. [e] In dichloromethane, scan rate = 50 mV s^{-1}; $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potential. [f] $\Delta E_p = E_{pa} - E_{pc}$.

Therefore, the oxidative response is metal-centered. The rather high positive potentials required for vanadium(IV)/vanadium(V) oxidation points to the high stability of the V^{4+} state in these complexes. Reluctance of the complexes to undergo reduction to the V^{3+} state is amply reflected in the fact that none of the complexes are reduced to V^{3+} even at the fairly high negative potential of −1 V. The above observations point to the rather exceptional stability of the V^{4+} state in these complexes in spite of its "bare" or non-oxo character and emphasize the high selectivity of the diacidic tetradentate chelating character of the present ligand systems in general for the "bare" or non-oxo V^{4+} acceptor center. This is also evident from preparative procedures given in Scheme 1 in which non-oxovanadium(IV) VL_2-type complexes are shown to be obtainable from various starting materials containing oxovanadium(IV) and -(V).

Concluding Remarks

The ligands used in this study appear to have special affinity for the non-oxo V^{4+} center manifested in the facile synthesis of VL_2-type complexes from various simple and complex oxovanadium(IV) and -(V) compounds as shown in Scheme 1. It is thought that the simultaneous charge satisfaction and formation of eight strong covalent bonds between the hard acceptor V^{4+} and the hard donor (O and N) points of the ligand is the basic reason for the exceptional stability of the VL_2 complexes. A noteworthy feature of the present work is the general nature of the synthetic procedure adopted for the design and synthesis of the ligands and the corresponding $V^{IV}L_2$-type complexes. This work opens up a new avenue in vanadium chemistry and furnishes a general route to the synthesis of octacoordinated non-oxovanadium(IV) complexes, which are quite scarce.

Acknowledgment. M.S. is grateful to the Council of Scientific and Industrial Research (New Delhi, India) for the award of a senior research fellowship. We thank EPSRC and the University of Reading for funds for the image plate system. We are grateful to Dr. A. K. Pal, former Professor at the Department of Solid State Physics, IACS, Kolkata 700 032, India, for fruitful discussion on the EPR.

Supporting Information Available: Representative cyclic voltammogram, EPR spectrum, mass spectrum, thermogravimetric/differential thermal analysis curve for complex **1**, and crystallographic data in CIF format for the structural analysis of the complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC062242R