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Synthesis, Characterization, and Reactivity of Mononuclear O,N-Chelated Vanadium(IV) and -(III) Complexes of Methyl 2-Aminocyclopent-1-ene-1-dithiocarboxylate Based Ligand: Reporting an Example of Conformational Isomerism in the Solid State

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Vanadium(IV) and -(III) complexes of a tetradentate N_2OS Schiff base ligand H_2L [derived from methyl 2-((β-aminoethyl)amino)cyclopent-1-ene-1-dithiocarboxylate and salicylaldehyde] are reported. In all the complexes, the ligand acts in a bidentate (N,O) fashion leaving a part containing the N,S donor set uncoordinated. The oxovanadium-(IV) complex $[VO(HL)_2]$ (**1**) is obtained by the reaction between $[VO(acac)_2]$ and H_2L. In the solid state, compound **1** has two conformational isomers **1a** and **1b**; both have been characterized by X-ray crystallography. Compound **1a** has the syn conformation that enforces the donor atoms around the metal center to adopt a distorted tbp structure ($\tau = 0.55$). Isomer **1b** on the other hand has an anti conformation with almost a regular square pyramidal geometry ($\tau = 0.06$) around vanadium. In solution, however, **1** prefers to be in the square pyramidal form. A second variety of vanadyl complex $[VO(L_{cyclic})_2](I_3)_2$ (**2**) with a new bidentate O,N donor ligand involving isothiazolium moiety has been obtained by a ligand-based oxidation of the precursor complex **1** with iodine. Preliminary X-ray and FAB mass spectroscopic data of **2** have supported the formation of a heterocyclic moiety by a ring closure reaction involving a N–S bond. Vanadium(III) complex $[V(acac)(HL)_2]$ (**3**) has been obtained through partial ligand displacement of $[V(acac)_3]$ with H_2L. Compound **3** has almost a regular octahedral structure completed by two bidentate HL ligands along with an acetylacetonate molecule. Electronic spectra, magnetism, EPR, and redox properties of these compounds are reported.

Introduction

Vanadium occurs as an "essential trace" element in diverse living forms.[1−6] It plays active roles in many enzymatic reactions such as halogenation of organic substrate[2,5,6] and fixation of nitrogen through an alternative pathway.[2,7] Another important biological activity of vanadium is its insulin-mimetic response which can in vivo simulate the uptake and metabolism of glucose.[8] In order to gain an insight into the intricate roles of vanadium in biological system, it is advantageous to acquire information about the basic coordination chemistry of this metal employing a biologically

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relevant ligand donor set.[9] A good number of studies with model complexes incorporating the mimics of histidine nitrogen, tyrosine phenolate, and aspartic or glutamic acid carboxylate etc. have revealed interesting chemistry of this element in physiologically relevant oxidation states (+2 to +5) under assorted O/N donor environments.[10−19]

Unlike with O/N donor ligands, the coordination chemistry of vanadium with sulfur donor ligands has remained largely unexplored. Recent studies, however, have brought into focus the inhibitory role of vanadium-containing substrates for a number of enzymes containing a cysteinal thiolate group in their active sites.[20] For quite some time, we have been engaged in studying the chemistry of oxo−metalate complexes, including vanadium in a sulfur-containing ligand environment.[21−23] The underlying objective is to tune the electronic structure, if possible, of the central metal ion by changing the ligand donor sets so as to achieve a desired control on their oxo-transfer reactivity. A current spate of interest in vanadium−thiolate chemistry[24−28] has been a source of impetus to focus our attention in this direction. For this, we have chosen a tetradentate N_2OS Schiff base ligand methyl 2-[2-(salicylideneamino)ethylamino]cyclopent-1-ene-1-dithiocarboxylate (H_2L), which we[29] as well as others[30,31] have used in recent times to develop interesting chemistry with diverse metal ions. The dithiocarboxylate sulfur atoms of this and related ligands have ligating abilities like those of thiolate anion as supported by X-ray crystal structure analysis.[32−34]

Herein we report the chemistry of vanadium(IV) and -(III) with H_2L ligand which has acted as a bidentate O,N donor ligand in the present case, leaving the two other coordination sites N,S to stay away from coordination. However, this unusual binding mode of H_2L has led to the isolation of syn and anti conformers of the oxovanadium(IV) compound.

Experimental Section

Materials. All manipulations in the following preparations were carried out under a blanket of purified dinitrogen, unless stated otherwise. The ligand H_2L and the precursor complexes $[VO(acac)_2]$ and $[V(acac)_3]$ (Hacac = acetylacetone) were prepared following reported methods.[30,35,36] Solvents were purified and dried from appropriate reagents[37] and distilled under nitrogen prior to their use. All other chemicals were commercially available and used as received.

Preparation of Complexes. *syn*-$[VO(HL)_2]$ (1a). A solution of $[VO(acac)_2]$ (0.27 g, 1 mmol) in methanol (25 mL) was added dropwise to a stirred solution of H_2L (0.64 g, 2 mmol) in dichloromethane (25 mL). The resulting bluish-green solution was stirred for 1 h more, during which time the color of the solution changed to a moss-green shade. Addition of acetone at this stage precipitated a dirty green solid from the solution. It was filtered, washed with ether, and dried in a vacuum to get 0.56 g of the crude product.

The crude material was dissolved in a minimum volume of warm dichloromethane (ca. 10 mL) to yield a yellowish-green solution. It was filtered, and the filtrate was cooled to room temperature. To this was added acetone dropwise till the solution became cloudy, and, on cooling at 4 °C overnight, the solution deposited brown crystals. Yield: 0.36 g (51%). Anal. Calcd for $C_{32}H_{38}N_4O_3S_4V$: C, 54.46; H, 5.39; N, 7.94. Found: C, 54.39; H, 5.32; N, 7.98. IR (KBr disk): ν = 1615 (C⋯N), 1550 (C⋯O/phenolate), 975 cm^{-1} (V═O_t). μ_{eff}, 1.70 μ_B.

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Table 1. Crystal Data, Data Collection, and Refinement Parameters for the Complexes **1a**, **1b**, and **3**

	1a	**1b**	**3**
formula	$C_{32}H_{38}N_4O_3S_4V$	$C_{32}H_{38}N_4O_3S_4V$	$C_{37}H_{45}N_4O_4S_4V$
fw	705.9	705.9	789.0
T (K)	297	297	295
cryst size (mm)	0.15 × 0.23 × 0.25	0.075 × 0.18 × 0.36	0.07 × 0.23 × 0.52
cryst syst	tetragonal	monoclinic	triclinic
space group	$P4_32_12$ (No. 120)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	9.2588(13)	12.0408(13)	8.366(2)
b (Å)	9.2588(13)	6.3985(13)	12.958(2)
c (Å)	39.194(5)	22.5585(33)	18.767(2)
α (deg)			107.67(1)
β (deg)		104.31(1)	95.82(2)
γ (deg)			95.64(2)
V (Å^3)	3360(2)	1686.1(9)	1910(1)
Z	4	2	2
ρ_{calcd} (g cm^{-3})	1.395	1.390	1.371
F(000)	1476	738	828
radiation used	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	0.56	0.559	0.522
$2\theta_{max}$ (deg)	50	50	50
no. of indep reflns			
total	1813	3261	6698
obsd [$I \geq \sigma(I)$]	1535	1680	4132
no. of params	200	272	451
$R(F)$,[a] $R_w(F)$ (obsd reflns)	0.068, 0.052	0.064, 0.051	0.055, 0.048
$R(F^2)$, $R_w(F^2)$[b] (all reflns)	0.061, 0.106	0.083, 0.106	0.089, 0.103
GOF	1.53	1.38	1.19

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^4]^{1/2}$.

***anti*-[VO(HL)$_2$] (1b).** The crude variety of [VO(HL)$_2$] as prepared above was dissolved in excess dichloromethane (ca. 30 mL) at room temperature and filtered. Diethyl ether was added dropwise until the solution appeared cloudy and refrigerated overnight at 4 °C to obtain long and thin green crystals of the anti variety of [VO(HL)$_2$]. Yield: 0.39 g (55%). Anal. Calcd for $C_{32}H_{38}N_4O_3S_4V$: C, 54.46; H, 5.39; N, 7.94. Found: C, 54.51; H, 5.31; N, 7.94. IR (KBr disk): ν = 1615 (C⋯N), 1555 (C⋯O/phenolate), 1000 cm^{-1} (V═O$_t$). μ_{eff}, 1.71 μ_B.

[VO(L$_{cyclic}$)$_2$](I$_3$)$_2$ (2). To a hot acetonitrile solution of **1** (crude variety, 0.4 g, 0.57 mmol) was added excess iodine (0.76 g, 3 mmol), also dissolved in acetonitrile (20 mL). The resultant dark solution was heated under reflux for 1 h and filtered. The filtrate was concentrated to ca. 10 mL by rotary evaporation and then left to evaporate slowly in the air. After 5 h, the dark crystalline solid that deposited was filtered. It was recrystallized from acetonitrile and dried in a vacuum. Yield: 0.32 g (38%). Anal. Calcd for $C_{32}H_{36}N_4I_6O_3S_4V$: C, 26.21; H, 2.46; N, 3.82. Found: C, 26.50; H, 2.61; N, 3.80. IR (KBr disk): ν = 1610 (C⋯N), 1550 (C⋯O/phenolate), 1000 cm^{-1} (V═O$_t$). Λ_M(CH$_3$CN): 162 Ω^{-1} cm^2 mol^{-1}. μ_{eff}, 1.65 μ_B.

[V(acac)(HL)$_2$] (3). To a dichloromethane solution (15 mL) of the ligand H$_2$L (0.37 g, 1.16 mmol) was added dropwise with stirring a stoichiometric amount (0.2 g, 0.57 mmol) of [V(acac)$_3$] dissolved in methanol (15 mL). The resulting red solution was stirred for an additional 1 h and filtered. The filtrate was reduced to ca. 10 mL by rotary evaporation and finally chilled in a freezer (4 °C). A brick red microcrystalline compound was obtained within 8−10 h. It was filtered, washed with ether, and dried in a vacuum. Recrystallization from dichloromethane/hexane yielded a crystalline product. Yield: 0.27 g (60%). Anal. Calcd for $C_{37}H_{45}N_4O_4S_4V$: C, 56.34; H, 5.71; N, 7.11. Found: C, 56.46; H, 5.72; N, 7.20. IR (KBr disk): ν = 1610 (C⋯N), 1550 (C⋯O/phenolate), 1520 cm^{-1} (C⋯O + C⋯C/acetylacetonate). μ_{eff}, 2.81 μ_B.

X-ray Crystallography. Complexes 1a, 1b, and 3. Diffraction quality crystals of **1a**, **1b**, and **3** were grown by slow diffusion of acetone, diethyl ether, and *n*-hexane, respectively, into their corresponding dichloromethane solutions. The cell dimensions were determined from the setting angles of an Enraf-Nonius CAD-4 diffractometer fitted with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) for 25 centered reflections. Structure solutions were from *E*-maps (SIR92).[38] Refinements were on $|F|^2$ for all independent data. The hydrogen atoms of **1b** were located and refined isotropically, except for those of the methyl group which were included at calculated, updated positions. Hydrogen atoms of **1a** and **3** were all included at calculated positions [d(C−H) = 0.95 Å; B(H) = 1.2B_{eq}(C)]. The TEXSAN program suite[39] was used in all calculations.

For **1a**, systematic absences of reflections indicated that the space group is either $P4_32_12$ or $P4_12_12$. The structure solution in $P4_32_12$ showed that the molecule lay on a crystal dyad axis. A structure solution and refinement in the enantiomorphic space group $P4_12_12$ led to the same residuals and standard deviations, and the results for $P4_32_12$ were arbitrarily retained. For **1b**, the systematic absences and the centric distribution of intensities indicated the space group $P2_1/n$. Small absorption corrections based on azimuthal scans were applied. During refinement, it became clear that both the vanadium atom and the apical oxygen atom O(1) were in half-occupied sites on either side of a crystallographic inversion center. The unit cell dimensions and Laue symmetry were checked with crystals of the same and of a second batch, but there was no indication that the true cell had twice the volume with pseudo-halving of the electron density on one axis, or possessed other than monoclinic symmetry. Data were also collected from a crystal of the second batch and the structure solved. The same space group, structure, and disorder were found. For **3**, the space group $P\bar{1}$ was confirmed by the structure solution. Table 1 contains a summary of crystal data and the final residuals of the compounds **1a**, **1b**, and **3**.

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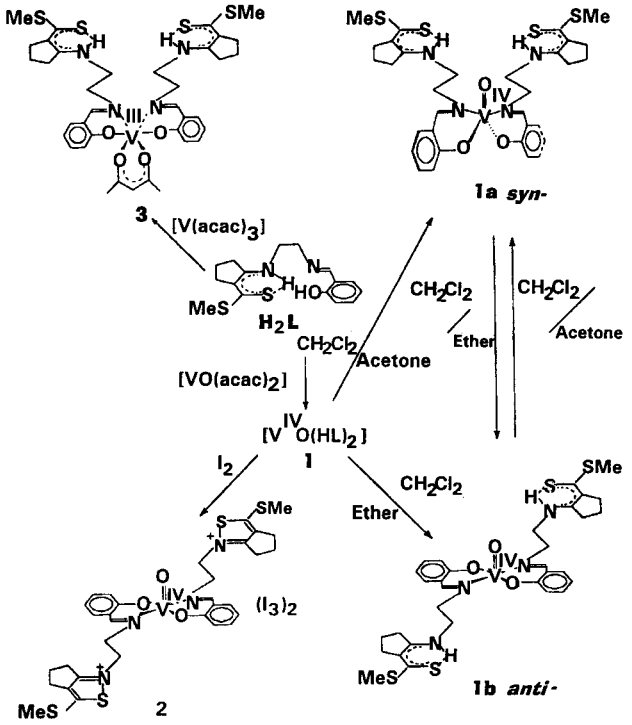
Scheme 1. Reaction Sequences for the Synthesis of the Complexes



Physical Measurements. Room temperature magnetic moments, UV−vis spectra, and IR spectra (as KBr disk) were obtained as described elsewhere.[22,23] X-band EPR spectra in DMF/toluene (1:10 v/v) at room temperature as well as in the frozen state (80 K) were recorded on a Varian E-line Century series instrument equipped with a Varian E-102 microwave bridge and an Oxford Instruments ITC-4 temperature controller. Positive ion fast atom bombardment (FAB) mass spectrometry was performed on a VG Pro/Spec eletrospray instrument.

Electrochemical measurements were performed with a PAR model 362 scanning potentiostat. Cyclic voltammograms were recorded at 25 °C in the designated solvent under dinitrogen 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 either a platinum or a glassy carbon working electrode, a Ag/AgCl reference electrode, and a platinum auxiliary electrode. Bulk electrolysis was carried out using a Pt-gauze working electrode. The ferrocene/ferrocenium (Fc/Fc^+) couple was used as the internal standard.[40]

Elemental analyses (for C, H, and N) were performed at IACS using a Perkin-Elmer 2400 analyzer.

Results and Discussion

Synthesis. The synthetic strategy is outlined in Scheme 1. The vanadyl complex (**1**) with composition $[VO(HL)_2]$ is obtained as dichroic crystals, green to brown in appearance, by the metathetical reaction involving $[VO(acac)_2]$ and H_2L. From this crude mixture, we have been able to isolate two conformers, **1a** and **1b**, by choice of solvent for recrystallization. The syn conformer **1a** has been isolated as shining brown crystals using a solvent mixture of CH_2Cl_2/acetone, while the anti conformer **1b** has been obtained as green needles using CH_2Cl_2/Et_2O as the solvent combination. Apart from differing conformations, these two isomers also differ in their geometries around the vanadium center. As will be seen, **1a** has a distorted trigonal bipyramidal geometry, while **1b** possesses a regular square pyramidal structure. In solution, however, only one of these two forms exists as indicated by EPR, IR, and electronic spectroscopic studies (see later).

The oxovanadium(IV) complex **2** has been synthesized by the oxidation of the precursor complex **1** with excess iodine. Iodine presumably attacks the sulfur atom of the dithiocarboxylate moiety to initiate the oxidation process. Interestingly, Hills and co-worker[41] have reported the formation of a mixed-valence dinuclear V(IV/V) compound $[(salen)V^{IV}-O-V^{V}(salen)=O]I_5$ from $[VO(salen)]$ (H_2salen = *N*,*N*′-bis(salicylidene)ethane-1,2-diamine) using iodine as the oxidant. Although complex **1** contains the bis-salicylaldiminato moiety similar to [VO(salen)], an altogether different reaction takes place in the present case, resulting in oxidation of the coordinated ligand with formation of an isothiazolium ring, as revealed by the X-ray structure of a poorly diffracting crystal.[42] Similar cationic heterocyclic species containing quarternary nitrogen centers are not uncommon in the literature.[43] The dipositive charge of the cationic complex species is balanced by two I_3^- anions. By contrast, the reaction between the free ligand H_2L and iodine affords a dark intractable material of unknown composition. The vanadium(III) complex $[V(acac)(HL)_2]$ (**3**) is obtained as red-brown crystalline solids by partial replacement of acetylacetonate from $[V(acac)_3]$. It should be noted that irrespective of the ratio of the reactants used, $[V(HL)_3]$ could not be isolated.

The oxovanadium compounds (**1a** and **1b**) are air-stable solids, moderately soluble in common organic solvents. In solution also they are fairly stable and undergo slow decomposition only on prolonged standing. Compound **2** is intensely dark colored. It has appreciable solubility in DMF and dissolves to a limited extent in acetonitrile. The vanadium(III) complex (**3**) is indefinitely stable in the solid state when stored under nitrogen and has moderate to high solubility in CH_2Cl_2, benzene, and DMF.

Some prominent IR band frequencies of the reported compounds are provided in the Experimental Section. Each of the compounds shows spectral features characteristic of the coordinated salicylaldiminato moiety. Of particular interest are the spectroscopic features of the conformers **1a** and **1b** in the 1100−850 cm^{-1} region (Figure 1) which, after screening the bands due to ligand internal stretchings, reveal interesting differences in their metal−terminal oxygen ($V=O_t$) vibrational modes. For the syn conformer **1a**, in which vanadium has a distorted tbp structure, the terminal $\nu(V=O_t)$ stretch is significantly shifted to a lower frequency, 975 cm^{-1}, relative to that of the anti conformer **1b**, 1000 cm^{-1}, where the geometry around vanadium is square pyramidal. Similar shifts, though less pronounced, of $\nu(V=O_t)$ have been

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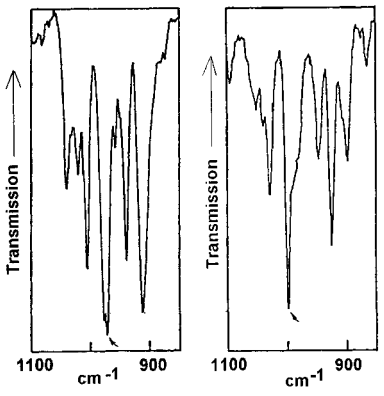

Figure 1. Relevant region (1100−850 cm^{-1}) of the IR spectra (in KBr disk) of **1a** (left) and **1b** (right), showing the shift in the $\nu(V{=}O_t)$ stretching modes.

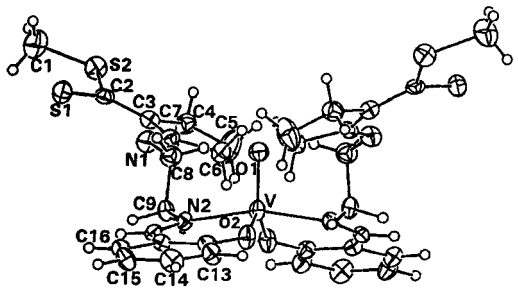

Figure 2. Molecular structure and atom-numbering scheme for **1a** with thermal ellipsoids drawn at the 30% probability level.

reported recently for a group of vanadyl complexes with geometries varying from square planar to distorted tbp structures.[14] Compound **2** also displays a $V{=}O_t$ stretch at about 1000 cm^{-1} corroborating the presence of oxovanadium-(IV).

Description of the Crystal Structures. Figures 2 and 3 display the perspective views of the isomeric complexes **1a** and **1b**, respectively. Their selected metrical parameters are given in Table 2. In both the complexes, the ligands bind in bis-bidentate (O,N) fashion and together with a terminal oxo ligand complete the metal coordination sphere. The appended part of the ligand with N,S donor sites, which stays away from coordination, plays the crucial role to attain the desired conformation. Thus in **1a**, the two appended parts are projected in the same direction (syn conformation), along the V═O terminal bond as reference (Figure 2), while in **1b** they are projected in the opposite directions relative to the V═O bond axis, thus generating the anti conformation (Figure 3).

Apart from differing conformations, the isomers also have different geometries about the metal center. In **1a**, the V and apical O atoms lie on a crystallographic 2-fold rotation axis which relates O(2) to O(2^i) and N(2) to N(2^i). The basal N_2O_2 is not planar, the O atoms being displaced away from V and the N atoms toward V, so that the geometry is somewhat distorted from square pyramidal toward trigonal bipyramidal ($\tau = 0.55$). There is no disorder in this molecule. By contrast, in isomer **1b** (Figure 3) the two organic ligands are related by a crystallographic center of symmetry, so that the N_2O_2 ligand set is exactly planar, but the VO(1) group lies on half-occupied sites related by the center of symmetry on either

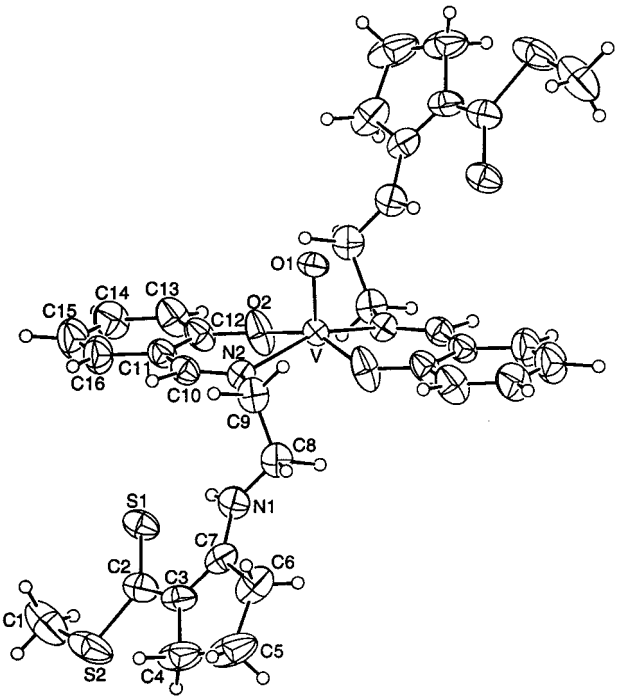

Figure 3. Perspective drawing of **1b** showing the atom-labeling scheme. The ellipsoids represent a 30% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1a** and **1b**

	1a	**1b**
V−O(1)	1.596(6)	1.577(4)
V−O(2)	1.914(4)	1.896(3)
V−O(2^i)		1.763(3)
V−N(2)	2.100(4)	2.189(3)
V−N(2^i)		2.064(3)
O(1)−V−O(2)	114.5(1)	103.1(2)
O(1)−V−O(2^i)		104.1(2)
O(1)−V−N(2)	98.2(1)	101.2(2)
O(1)−V−N(2^i)		102.1(2)
O(2)−V−N(2)	88.0(2)	84.0(1)
O(2^i)−V−N(2^i)		86.7(1)
N(2)−V−N(2^i)	163.6(3)	156.4(1)
O(2)−V−O(2^i)	131.0(3)	152.5(1)
O(2)−V−N(2^i)	85.2(2)	87.2(1)
V−N(2)−C(9)	119.4(4)	118.1(3)
V−N(2^i)−C(9^i)		122.3(3)
V−N(2)−C(10)	123.8(4)	123.1(3)
V−N(2^i)−C(10^i)		119.8(3)
N(2)−C(9)−C(8)	109.5(5)	110.8(4)

side of the N_2O_2 plane. Thus, the geometry appears accurately square pyramidal ($\tau = 0.06$) but with disorder.

In complex **1a**, the two imino nitrogen atoms are trans to each other, occupying the axial sites of a tbp with the N(2)−V−N(2^i) angle being 163.6(3)°. The two phenolate oxygen atoms O(2) and O(2^i) along with the terminal oxo ligand O(1) form the trigonal basal plane. The central V atom lies exactly on the plane, and N(2) and N(2^i) atoms are at the same distance away, 2.100(4) Å, from V. On the other hand, in **1b** the two phenolate oxygens and the two imino nitrogens are mutually trans to each other. The vanadium atom is displaced by 0.430 Å from the mean square plane N(2)N-(2^i)O(2)O(2^i) toward the apical oxo atom O(1). The terminal V−O(1) distances of 1.596(6) Å in **1a** and 1.577(4) Å in **1b** are typical of five-coordinate vanadyl compounds.[44] Of

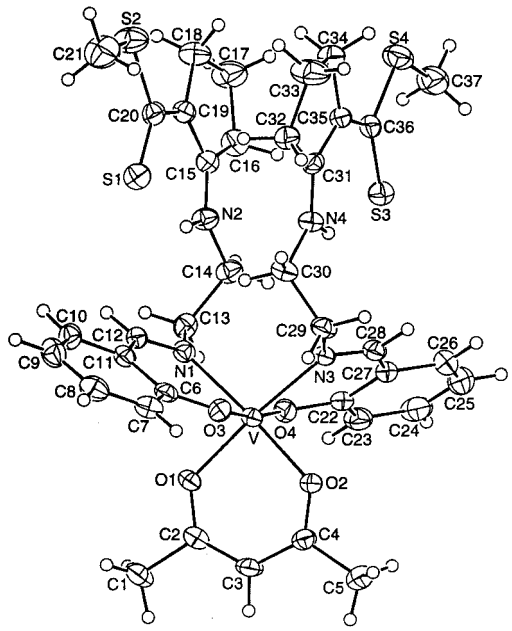

Figure 4. Molecular structure and atom-numbering scheme for **3**. The ellipsoids represent a 30% probability.

particular interest are the vanadium donor distances of the two HL ligand units in the two conformers which show interesting variations (Table 2). In **1a**, the distances 1.914(4) Å ($V-O_{phenoxo}$) and 2.100(4) Å ($V-N_{imino}$) are in the range expected for salicylaldiminato−vanadyl complexes.[14] In the case of **1b,** however, the 50/50 possibility that the VO unit is pointing either "up" from the N_2O_2 basal plane or "down" means that in either orientation the complex taken as a whole lacks any crystallographic symmetry so that the distances pertaining to the two sets of HL are different. The $V-O_{phenoxo}$ distance (V−O2, 1.896(3) Å) with the first ligand and the $V-N_{imino}$ distance ($V-N2^{i}$, 2.064(3) Å) from the second ligand are in the expected range,[14] while the remaining two distances are either relatively shorter ($V-O2^{i}$, 1.763(3) Å) or longer (V−N2, 2.189(3) Å) than the expected range.[14] Steric requirement(s) of the anti conformation in **1b** probably forces the ligand pair to behave in such a manner.

The structure of complex **3** consists of a discrete $[V(acac)(HL)_2]$ species, with the ORTEP diagram shown in Figure 4. Selected interatomic distances and angles are listed in Table 3. The coordination sphere (N_2O_4) about the vanadium atom consists of a chelated acetylacetonate molecule (O1 and O2) and two monodeprotonated HL ligands acting in a bidentate fashion as in **1a** and **1b**, contributing two phenolate oxygens (O3 and O4) and two iminic nitrogen atoms (N1 and N3) to provide an almost regular octahedral environment around the metal center. V, O1, N1, N3, and O2 are coplanar, and the angles within the plane lie in the range 85.1(1)°−99.5(1)°. The trans angles O3−V−O4 (171.2(1)°), O2−V−N1 (175.3(1)°), and O1−V−N3 (174.7(1)°) are close to linearity. The $V-O_{phenoxo}$ (1.927(3) and 1.915(3) Å) and $V-N_{imino}$ distances (2.145(3) and 2.151(3) Å) are similar to those observed in other salicylaldiminato−vanadium(III) complexes.[45] The slightly elongated V−O1 (1.996(2) Å) and V−O2 (1.989(2) Å) distances from the acetylacetonate ligand are also close to the values reported for related vanadium(III) complexes.[46]

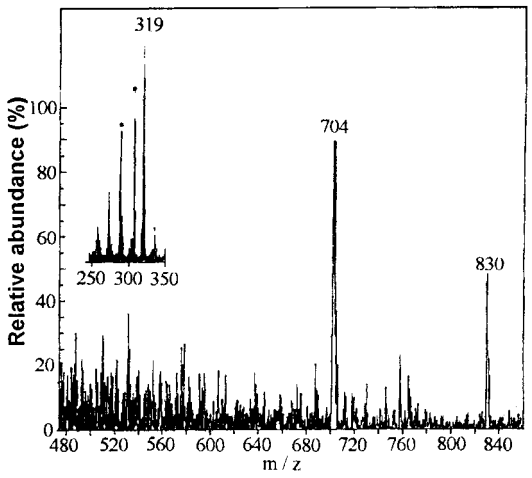

Figure 5. Positive-ion FAB mass spectrum of **2** in *m*-nitrobenzyl alcohol matrix. Asterisks indicate matrix impurities.

Table 3. Inter Atomic Distances (Å) and Angles (deg) Relevant to the Vanadium Coordination Sphere for Complex **3**

	Bond Lengths (Å)		
V−O(1)	1.996(2)	V−O(2)	1.989(2)
V−O(3)	1.927(3)	V−O(4)	1.915(3)
V−N(1)	2.145(3)	V−N(3)	2.151(3)
	Bond Angles (deg)		
O(1)−V−O(2)	89.7(1)	O(2)−V−N(3)	85.1(1)
O(1)−V−O(3)	92.2(1)	O(3)−V−O(4)	171.2(1)
O(1)−V−O(4)	94.2(1)	O(3)−V−N(1)	86.9(1)
O(1)−V−N(1)	85.8(1)	O(3)−V−N(3)	87.6(1)
O(1)−V−N(3)	174.7(1)	O(4)−V−N(1)	87.6(1)
O(2)−V−O(3)	94.7(1)	O(4)−V−N(3)	86.5(1)
O(2)−V−O(4)	91.3(1)	N(1)−V−N(3)	99.5(1)
O(2)−V−N(1)	175.3(1)		

Mass Spectrometry. Positive ion fast atom bombardment (FAB) mass spectroscopic data for **2** have been recorded (in *m*-nitrobenzyl alcohol matrix) to establish its complex stoichiometry. Figure 5 displays the spectrum that involves peaks with the correct isotopic distribution and expected mass for the molecular ion and its fragments. The peaks at *m*/*z*, 830 and 704, correspond to $[VO(L_{cyclic})_2]I^+$ and $[VO(L_{cyclic})_2]-H^+$, respectively. The peak at *m*/*z*, 319 (shown in the inset of Figure 5), seems to be due to the free $(HL_{cyclic})^+$ ligand moiety.

Magnetism and EPR. The room temperature magnetic moments of **1a**, **1b**, and **2** are given in Table 4. All the oxovanadium(IV) complexes have moments in the range 1.65−1.71 μ_B as expected for a simple $S = {}^1/_2$ paramagnet, while the value 2.81 μ_B for **3** is close to the spin-only moment (2.83 μ_B) expected for d^2 vanadium(III) complexes.

X-band EPR spectra of the vanadium(IV) complexes **1a**, **1b**, and **2** were recorded in solution (DMF/toluene, 1:10 v/v) both at room temperature (298 K) and in the frozen state

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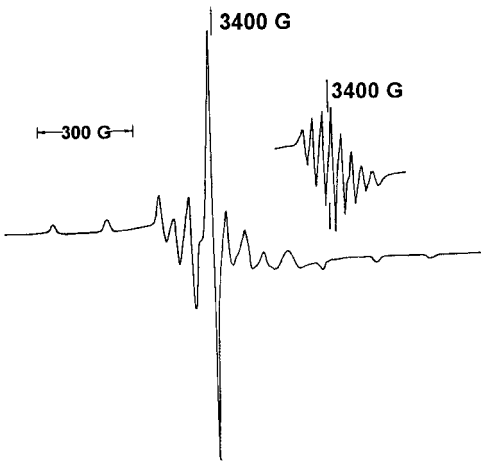

Figure 6. Frozen solution X-band EPR spectrum (80 K) of **1a** in DMF/toluene (1:1 v/v): frequency, 9.50 GHz; gain, 6.3×10^3. The inset shows the room temperature (298 K) EPR spectrum of the same solution: frequency, 9.7 GHz; gain, 1.25×10^3.

Table 4. Magnetic Moment and EPR Data for the Oxovanadium(IV) Complexes

compd	$\mu_{eff}{}^a/\mu_B$	$\langle g\rangle^b$	$10^4\langle A\rangle^b/\text{cm}^{-1}$	$g_{\|}{}^c$	$g_{\perp}{}^c$	$10^4A_{\|}{}^c/\text{cm}^{-1}$	$10^4A_{\perp}{}^c/\text{cm}^{-1}$
1a	1.70	1.973	87.7	1.947	1.978	161.3	49.0
1b	1.71	1.973	87.3	1.944	1.980	161.5	49.2
2	1.65	1.993	86.1	1.978		161.6	

[a] Measured at room temperature with powdered polycrystalline sample. [b] From room temperature spectra in DMF/toluene (1:10 v/v) solution. [c] From frozen solution (80 K) spectra.

(80 K). A representative frozen solution spectrum (**1a**) is shown in Figure 6, which reveals well-resolved axial anisotropy with 16-line hyperfine structure, characteristic of an interaction of vanadium nuclear spin (^{51}V, $I = {}^7/_2$). The observed **g**-tensor parameters (Table 4) are $g_{\|} = 1.947$ ($A_{\|} = 161.3 \times 10^{-4}$ cm^{-1}) and $g_{\perp} = 1.978$ ($A_{\perp} = 49.0 \times 10^{-4}$ cm^{-1}). The same solution of **1a** at room temperature displays typical 8-line isotropic signals (Figure 6, inset) with $\langle g\rangle = 1.973$ and $\langle A\rangle = 87.7 \times 10^{-4}$ cm^{-1}. As given in Table 4, there is a close agreement between the spectral parameters obtained at room temperature and in the frozen state [$\langle g\rangle = (1/3)(g_{\|} + 2g_{\perp})$ and $\langle A\rangle = (1/3)(A_{\|} + 2A_{\perp})$], which clearly indicates that over the temperature range 298−80 K the electronic structure of **1a** remains unaffected in solution. Virtually identical spectra were obtained for the isomer **1b** (Table 4), indicating the presence of a single conformer in solution at least in the time scale of EPR spectroscopy.

Compound **2** exhibits an axial spectrum in the frozen solution, which is resolved to the extent to provide the parameters: $g_{\|} = 1.978$ and $A_{\|} = 161.6 \times 10^{-4}$ cm^{-1}. A comparison of the data in Table 4 reveals that the **g**-tensor parameters for **1a** and **1b** are less than the corresponding values of compound **2**, indicating that the unpaired electron in both cases are not located in the orbitals of identical composition (with respect to delocalization of the d electron toward the ligand donor atoms). The vanadium(III) compound **3** is EPR silent.[47]

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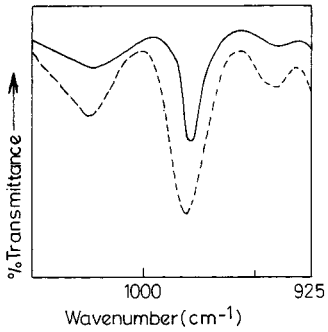

Figure 7. Infrared spectra of **1a** (—) and **1b** (− − −) in dichloromethane solution.

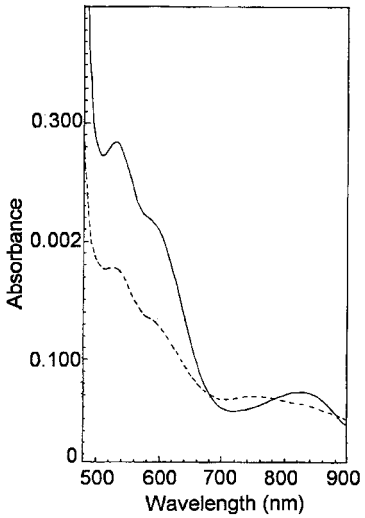

Figure 8. Electronic absorption spectra of **1a** (- - -) and **1b** (—) in DMF (concentration 3.15×10^{-3} M) and dichloromethane solution (concentration 4.45×10^{-3} M), respectively.

Table 5. Summary of Electronic Spectral Data in Solution

complex	solvent	λ_{max}/nm (ϵ_{max}/mol^{-1} cm^2)
1a	DMF	736 (25), 600 (44), 531 (63), 400 (25000), 320 (12500), 240 (27200)
1a	CH_2Cl_2	840 (21), 606 (sh), 531 (64), 399 (27700), 316 (13700), 239 (26600)
1b	DMF	740 (19), 604 (sh), 528 (61), 398 (25300), 314 (14450), 240 (27300)
1b	CH_2Cl_2	825 (16), 600 (48), 531 (64), 400 (25700), 316 (12800), 240 (27000)
2	CH_3CN	535 (sh), 373 (38200)
3	CH_2Cl_2	530 (sh), 400 (23250), 316 (14550), 259 (14400), 237 (22450)

Spectroscopic Studies in Solution. In solution, infrared spectral features of **1a** and **1b** are virtually identical. Figure 7 displays the relevant region (925−1050 cm^{-1}) of the spectra taken in dichloromethane. The ν(V═O$_t$) stretch for both the isomers appears at 980 cm^{-1}, indicating their identical geometry in solution, unlike in the solid state.

The solution absorption spectral data for the complexes are given in Table 5. For the isomers **1a** and **1b**, the spectra have been recorded in DMF and dichloromethane. In each solvent, the spectral features of the individual isomers are almost identical and show only a marginal change in going from one solvent to the other. Figure 8 displays the spectra of **1a** and **1b**, recorded in DMF and dichloromethane, respectively. In the 900−500 nm range, each of these spectra

exhibits three prominent ligand-field bands of low intensities ($\epsilon = 16-64$ mol^{-1} cm^2) which are most likely due to $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$, and $^2B_2 \rightarrow {}^2A_1$ transitions under idealized C_{4v} symmetry.[48] The observed change in the position of the lowest energy d−d band due to solvent effect is not unusual for square pyramidal vanadyl complexes.[48b] The results lend support to the fact that the square pyramidal isomer (**1b**) appears to be the preferred geometry of **1** in solution.

The remaining compounds (**2**, **3**), including the vanadium(III) complex (**3**), display a single d−d absorption feature in the form of a shoulder at ca. 535 nm. In the UV region a high-intensity band observed at almost 400 nm in the complexes is probably due to a ligand-to-metal charge-transfer (LMCT) transition, while the other bands at still higher energies are due to ligand-internal transitions.

Electrochemistry. The redox behavior of the complexes was investigated by cyclic voltammetry using a platinum or glassy carbon working and Ag/AgCl reference electrode. Complex **3** in CH_2Cl_2 with a glassy carbon electrode exhibits a single electrochemical response involving V(III)/V(IV) electron transfer in the potential window −1.5 to 1.5 V with quasi-reversible features, $E_{1/2} = 0.59$ V vs Ag/AgCl and $\Delta E_p = 110$ mV. Controlled potential coulometric experiments using a platinum gauze working electrode have confirmed the one-electron stoichiometry of the electron-transfer process (eq 1).

$$[V^{III}(acac)(HL)_2] \rightleftharpoons^{-e^-} [V^{IV}(acac)(HL)_2]^+ \qquad (1)$$

The cyclic voltammogram of **2** in CH_3CN with a platinum working electrode shows the presence of an irreversible oxidation process (E_{pa}, 0.31 V) followed by a reversible redox couple ($E_{1/2}$, 0.59 V vs Ag/AgCl). Since the I_3^- anion in this complex itself is electrode active, spiking of a solution of **2** with $[NMe_4][I_3]$ led to an increase of the peak currents, while showing no effect on the redox potentials of the couples in the voltammogram, thus confirming their I_3^- anion dependence. The isomeric vanadyl complexes **1a** and **1b** are found to be electrochemically inactive.

Concluding Remarks

Compounds **1a** and **1b** constitute rare examples of conformational isomers observed in the solid state with discrete molecules of coordination compounds.[49] Vanadium centers in these molecules have pentacoordination environments completed by a terminal oxo ligand and two salicylaldiminato moieties (N_2O_2) from a pair of coordinated HL ligands. Compounds of this type mostly have distorted geometries intermediate between the idealized square pyramidal and trigonal bipyramidal extremes;[14] the degree of trigonality in such a system may be quantified using a structural index parameter (τ) which may vary from zero for a regular tetragonal to unity when the geometry is purely trigonal.[50] The syn and anti conformations in the present molecules are likely to preset the conditions needed so that the coordination geometry around vanadium is a distorted trigonal bipyramid ($\tau = 0.55$) in **1a** and an almost regular square pyramid ($\tau = 0.06$) in **1b**. In solution, however, **1** exists as a single isomer, probably in the square pyramidal form (**1b**) with C_{4v} symmetry, as indicated by IR and electronic spectroscopy. Results of EPR spectroscopy seem to support this hypothesis, since the additivity relationships commonly applied to the interpretation of vanadium(IV) EPR spectra may possibly be more accurate for the square pyramidal complexes than for trigonal bipyramidal complexes.[51]

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Supporting Information Available: Three X-ray crystallographic files for compounds **1a**, **1b**, and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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