

Chemistry of mononuclear and mixed valence binuclear oxovanadium chelates incorporating ONO-hydrazone ligands

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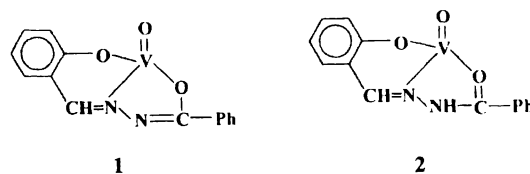
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The dark coloured complex of type $[V^V_2O_3(L)_2]$ has been synthesized in excellent yields by reacting bis(acetylacetonato)oxovanadium(IV) with H_2L in the presence of air in acetone. In presence of small amount of water $[V^VO_2(HL)]$ is isolated. Electronic and IR spectra as well as the metal reduction potentials of the complexes are reported. In crystalline $[V^VO_2(HL)]$ the vanadium(V) has a distorted square-pyramidal geometry where the ligands bind as a tridentate monoionised form. The C-N and C-O bond lengths around the chelate rings are consistent with the ketonic description of the ligand. The O-V-O bond angle is greater than 107° which is a characteristic feature of the VO_2^+ complexes with pentacoordinate vanadium. In the crystal lattice the $[V^VO_2(HL)]$ molecule forms a dimer via intermolecular N...O hydrogen bonding. The green coloured complex $Et_4N[V_2O_3(L)_2]$ has been synthesized in almost quantitative yields by one electron reduction of $[V^V_2O_3(L)_2]$ (at ~ 0.0 V vs SCE) in dichloromethane solution containing tetraethylammonium perchlorate. The complex $Et_4N[V_2O_3(L)_2]$ is characterized by electronic, IR and EPR spectroscopic methods. The isotropic solution spectra of the complex consists of 15 lines ($A \sim 50$ G; and $g \sim 1.950$) revealing the delocalization of the unpaired electron over the two equivalent metal centers. The EPR spectra in the frozen state is consistent with the localization of the unpaired electron in one center ($A_{||} \sim 174$ G; $A_{\perp} \sim 74$ G; $g_{||} \sim 1.950$ $g_{\perp} \sim 1.960$).

The recent interest in the coordination chemistry of oxovanadium(V) in O, N coordination environment is mainly due to the discovery that the vanadium is an essential element in biological system¹⁻⁵. The metal complexes participate in different enzymatic reaction such as haloperoxidation⁶⁻⁹, nitrogen fixation¹⁰⁻¹³ and catecholase activity^{14,15}, as well as insulin mimetic properties¹⁶⁻²⁰. Other areas of chemistry of vanadium span in the catalytic activity (in organic synthesis)²¹⁻²³, and magneto-structural study of polynuclear species^{24,25}, also received significant attention.

This has prompted us to search for a new family of oxovanadium(V) species using tridentate ONO donor hydrazones. It has been documented that it binds to VO^{3+} as in deionised form as in **1**²⁶⁻²⁸. In this present work we are interested in the synthesis and characterization of a group of interrelated chelates incorporating $V^VO_2^+$, $V^V_2O_3^{4+}$ and $V_2O_3^{3+}$. In the case of $V^VO_2^+$, the ligand binds in an unpredicted tautomeric form as in **2**. Another notable feature is that studies on electrogenerated $V^V V^{IV} O_3^{3+}$ species from its congeners $V^V_2O_3^{4+}$ are rare²⁹⁻³¹. Thus the usefulness of electron delocalized nature of mixed-valence $V^V V^{IV} O_3^{3+}$ has in turn mobilized us to synthesize and characterize a new family of $V^V V^{IV} O_3^{3+}$ species. One representative complex of type

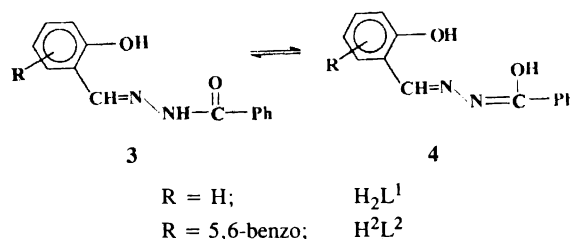
$V^VO_2^+$ has also been structurally characterized. Metal redox and spectral properties of all the new complexes are scrutinized in this work.



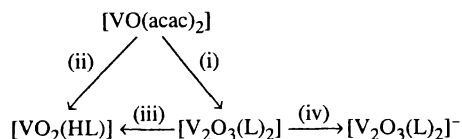
Results and discussion

Synthesis and spectra :

Two tridentate hydrazone ligands H_2L^1 and H_2L^2 (general abbreviation, H_2L) may exist in the form **3** and **4** have been used in the present work. The ligands have been prepared by the condensation of salicylaldehyde/2-hydroxy-naphthaldehyde with benzoylhydrazine.



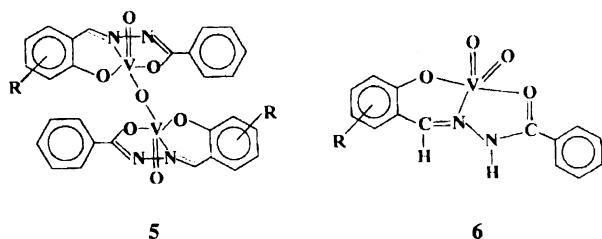
The syntheses of complexes are summarized in Scheme 1.



- (i) Reflux for 30 min in acetone or acetonitrile in air.
 (ii) Stir for 3 h in air in acetone or acetonitrile in the presence of small amount of water.
 (iii) Stir for 6 h in air in acetone or acetonitrile in the presence of small amount of water.
 (iv) Electroreduction.

Scheme 1

The reaction of bis(acetylacetonato)oxovanadium(IV) with stoichiometric amounts of hydrazone ligands in acetone or acetonitrile solution in air afforded a dark coloured crystalline solids, $[V^V_2O_3(L)_2]$, **5** in excellent yields. In the presence of small amount water, yellow coloured mononuclear $[V^VO_2(HL)]$, **6** is obtained. Upon electroreduction of $[V^V_2O_3(L)_2]$ it furnishes mixed-valence($V^{IV}V^V$) analog both in solid and solution.



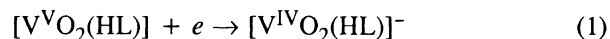
The IR spectra of the complex $[V^V_2O_3(L)_2]$, **5**, do not display any stretch at 3300 cm^{-1} (OH), at 3100 cm^{-1} (NH) and at 1675 cm^{-1} ($C=O$)³². A strong peak with a shoulder observed at 1605 cm^{-1} for the complex is possibly due to the conjugate $C=N-N=C$ moiety of the coordinated ligands³³. Thus, in the complex the amide functionalities of the ligands exist in the enolate form and acts as a dibasic phenolate-O, imine-N and deprotonated amide O-donor. On the other hand in case of **6**, a broad N-H stretching vibration are observed at about 3400 cm^{-1} and a sharp band near 1700 cm^{-1} due to the presence of ketonic $C=O$ function. Both **5** and **6** display a strong terminal $V=O$ stretch near $\sim 1000\text{ cm}^{-1}$. An additional sharp peak is observed at 650 cm^{-1} in case of **6** which was believed to be appear due to $V-O-V$ vibration^{29,31}.

The electronic spectra of vanadium(V) complexes con-

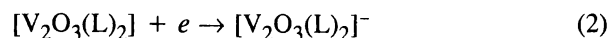
sists of several bands in the region 300–500 nm. The band near 400 nm is believed to be of the $L^{2-}/HL^{1-} \rightarrow V$ charge transfer transition and the band near 300 nm is most probably due to intraligand transition²⁹.

Metal redox : mixed valence $[V^V V^{IV}O_3(L)_2]$:

All the complexes are electroactive at platinum electrode. The complex $[V^VO_2(HL)]$ shows a quasireversible cyclic voltammetry peak near +0.40 V vs SCE in dimethylsulfoxide solution. This peak was assigned as $[V^VO_2(HL)]-[V^{IV}O_2(HL)]^-$ couple (eq. (1)),



The $[V_2O_3(L)_2]$ species also displayed a quasireversible cyclic voltammetric response near +0.26 V vs SCE in dichloromethane solution which was logically assigned as $[V_2O_3(L)_2]-[V_2O_3(L)_2]^-$ couple (eq. (2)),



Constant potential reduction at 0.00 V leads to quantitative formation of the one electron reduced complex, $[V_2O_3(L)_2]^-$ and upon oxidation at +0.30 V, it is fully regenerated $[V_2O_3(L)_2]$. The electrogenerated species show an additional band at 950 nm is assigned to the intervalence charge transfer transition³¹.

Crystal structures :

The structures of $[VO_2(HL^1)]$ has been determined. Molecular views excluding the hydrogen atoms are shown in Fig. 1. Selected bond parameters and positional parameters are listed in Tables 1 and 2 respectively.

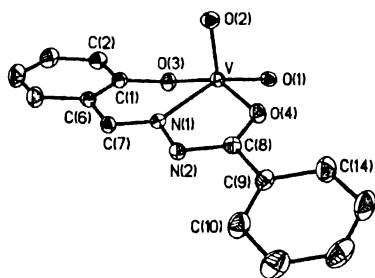
In $[V^VO_2(HL^1)]$ the ligand binds in a tridentate monoionised fashion. The oxygen atom of the benzoyl hydrazone part remains in ketonic form which is evident from the following facts : (i) the $C(8)-O(4)$ ($1.265(3)\text{ \AA}$)

Table 1. Selected bond lengths (\AA) and angles ($^\circ$) for $[VO_2(HL^1)]$

Bond lengths			
V-O(1)	1.642(2)	V-O(2)	1.616(2)
V-O(3)	1.893(2)	V-O(4)	2.037(2)
V-N(1)	2.156(2)	O(4)-C(8)	1.265(3)
N(2)-C(8)	1.322(3)	N(1)-N(2)	1.378(3)
O(3)-C(1)	1.330(3)		
Bond angles			
O(1)-V-O(2)	106.66(9)	O(1)-V-O(3)	100.76(9)
O(1)-V-O(4)	92.07(9)	O(2)-V-O(3)	100.98(9)
O(2)-V-O(4)	99.82(9)	O(3)-V-O(4)	151.19(8)
O(1)-V-N(1)	151.29(8)	O(2)-V-N(1)	100.21(9)
O(3)-V-N(1)	83.59(8)	O(4)-V-N(1)	73.26(8)

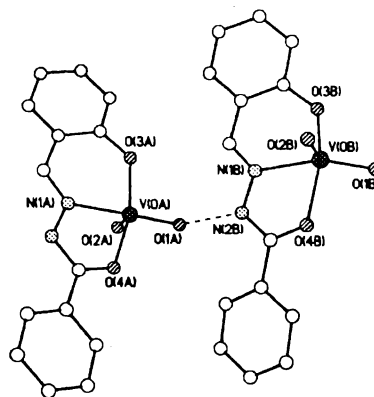
Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{V}^{\text{VO}}_2(\text{HL}^1)]$

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
V	-3(1)	451(1)	2497(1)	25(1)
O(1)	363(1)	389(1)	3906(1)	30(1)
O(2)	-76(1)	-1436(2)	2053(2)	36(1)
O(3)	-1319(1)	973(2)	2398(2)	33(1)
O(4)	1339(1)	1021(2)	2235(2)	33(1)
N(1)	-185(1)	1726(2)	864(2)	24(1)
N(2)	666(2)	2279(3)	595(2)	26(1)
C(1)	-2031(2)	1106(3)	1486(2)	30(1)
C(2)	-2967(2)	750(4)	1630(3)	40(1)
C(3)	-3729(2)	900(4)	722(3)	49(1)
C(4)	-3602(2)	1428(5)	-348(3)	54(1)
C(5)	-2692(2)	1810(4)	-516(3)	43(1)
C(6)	-1894(2)	1643(3)	389(2)	30(1)
C(7)	-968(2)	2087(3)	155(2)	29(1)
C(8)	1437(2)	1872(3)	1365(2)	28(1)
C(9)	2399(2)	2426(3)	1214(2)	31(1)
C(10)	2551(2)	3458(4)	344(3)	48(1)
C(11)	3469(2)	3998(5)	285(3)	60(1)
C(12)	4235(2)	3461(5)	1098(3)	59(1)
C(13)	4106(2)	2433(5)	1960(4)	60(1)
C(14)	3185(2)	1901(4)	2035(3)	48(1)

**Fig. 1.** ORTEP plot (30% probability ellipsoids) and atom labeling scheme for $[\text{V}^{\text{VO}}_2(\text{HL}^1)]$.

and C(8)–N(2) (1.322(3) Å) bond distances in the complex is in good agreement with ketonic chelation instead of enolic binding²⁷, (ii) the presence of N(2)–H also provides strong support for the ketonic form of the ligand in $[\text{V}^{\text{VO}}_2(\text{HL}^1)]$. The ligand HL^{1-} span meridionally forming a five-membered and a six-membered chelate ring. The $\text{V}(\text{HL}^1)$ fragment (excluding the pendant phenyl ring) consist of two planar parts C(1)–C(7), O(3) and V (mean deviation ~ 0.12 Å) and N1, N2, C8, O4 (mean deviation ~ 0.004 Å). The dihedral angle between the two planes is 12.5° .

The coordination environment of the complex is a distorted square pyramidal. The base is defined by the coordinated ONO atoms of the planar (mean deviation ~ 0.09 Å) L^{1-} ligand and an oxo oxygen atom. The other oxo oxygen atom occupies the apex of the pyramid. The metal atom is displaced by 0.35 Å toward the apical oxygen atom from the base. The hydrogen atom attached with N(2) is engaged in intermolecular hydrogen bonding with the basal oxo oxygen atom of the other molecule (N(2)....O(1) $\sim 2.724(6)$ Å) forming a dimer in the lattice (Fig. 2).

**Fig. 2.** Perspective view of $[\text{V}^{\text{VO}}_2(\text{HL}^1)]$ in the lattice showing the intermolecular N....O hydrogen bonds.

EPR Spectra : valence delocalisation in $[\text{V}^{\text{V}}\text{V}^{\text{IV}}\text{O}_3(\text{L})_2]^-$:

The magnetic moment at room temperature is $\sim 1.77 \mu_{\text{B}}$, corresponding to the presence of one unpaired electron and the complexes are EPR active both at room temperature and at 77 K. Resonance parameters are listed in Table 3 and a representative spectrum is shown in Fig. 3. Isotropic room temperature (300 K) solution, (in dichloromethane) spectra of $[\text{V}^{\text{V}}\text{V}^{\text{IV}}\text{O}_3(\text{L})_2]^-$ consist of 15 lines (Fig. 3) and it reveals that the unpaired electron is coupled with both the vanadium nuclei ($I = 7/2$) in solution at room temperature. On the other hand, the spectra at frozen temperature (77 K) consist of distinct parallel and perpendicular lines consistent with the presence of isolated axial $\text{V}^{\text{IV}}\text{O}$ centers^{34,35}. At this temperature (77 K) the unpaired electron is localized at a single center interacting with only one vanadium nucleus. Spectral parameters of the frozen solution correlate with the fluid solution as in eqs. (3) and (4)^{36,37},

$$A_{\text{av}} \approx 2 A_{\text{iso}} \quad (3)$$

$$g_{\text{av}} \approx g_{\text{iso}} \quad (4)$$

Table 3. X-Band EPR data

Complex	Matrix	g_{iso}	A_{iso}, G	g_{\parallel}	g_{\perp}	g_{av}^a	A_{\parallel}, G	A_{\perp}, G	$A_{\text{av}}^b, \text{G}$
$\text{Et}_4\text{N}[\text{V}_2\text{O}_3(\text{L}^2)_2]$	CH_2Cl_2 , 300 K	1.978	50.71						
	CH_2Cl_2 , 77 K			1.952	1.959	1.956	173.57	74.28	107.37

$$^a g_{\text{av}} = 1/3 [2g_{\perp} + g_{\parallel}], \quad ^b A_{\text{av}} = 1/3 [2A_{\perp} + A_{\parallel}].$$

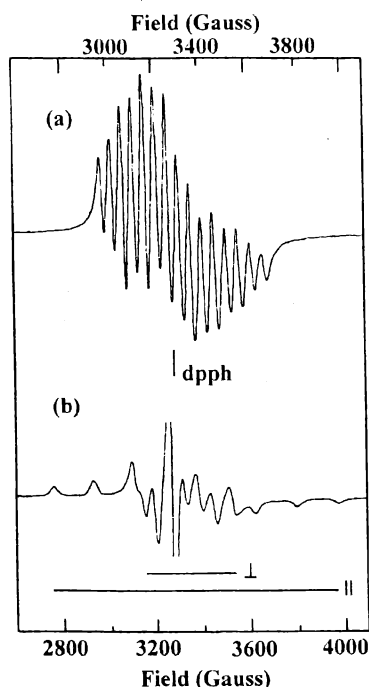


Fig. 3. EPR spectra at X-band of $\text{Et}_4\text{N}[\text{V}^{\text{IV}}\text{V}^{\text{VO}}_3(\text{L}^1)_2]$: (a) in dichloromethane/toluene glass at 77 K; (b) in dichloromethane at 298 K. Instrument settings: power 30 dB; modulation, 100 kHz; sweep centre, 3200 G; sweep width, 2000 G; sweep time, 240 s.

In such solution the unpair electron is delocalized over the two metal atoms at X-band EPR-time scale. Thus, the complex may suitably described as class II^{38,39} mixed-valence oxovanadium(IV/V) complex on X-band EPR time scale.

Conclusion:

The tridentate ONO hydrazone ligand H_2L has afforded pentacoordinate square pyramidal mononuclear $[\text{VO}_2(\text{HL})]$ and $[\text{V}_2\text{O}_3(\text{L})_2]$ dinuclear species. The main finding of the work is the binding mode of H_2L towards oxovanadium(V). In $[\text{VO}_2(\text{HL})]$ the ligand binds in the ketonic form whereas in $[\text{V}_2\text{O}_3(\text{L})_2]$ the ligand binds in enolate form. The dinuclear complex is reversibly electroreducible affording the mixed-valence $[\text{V}^{\text{IV}}\text{V}^{\text{VO}}_3(\text{L})_2]^-$ species both in solid and solution state.

In solid state the unpaired electron is localized at a single center whereas in solution the unpaired electron is delocalized between the two equivalent metal atoms.

Experimental

Materials:

Bis(acetylacetonato) oxovanadium(IV)⁴⁰ and tetraethylammonium perchlorate⁴¹ were prepared by reported procedures. CDCl_3 and $\text{DMSO}-d_6$ was obtained from Aldrich. All other chemicals and solvents were of analytical grade and were used as received.

Physical measurements:

Proton NMR spectra were recorded on a Bruker FT 300 MHz spectrometer, infrared spectra on a Perkin-Elmer 783 spectrometer and electronic spectra on a Hitachi 330 spectrophotometer. ^{51}V NMR Spectra were drawn on a Varian spectrometer (78.8 MHz) at 25°C, externally referenced to VOCl_3 . Electrochemical measurement was performed on a PAR model 370-4 system as described previously⁴². All potentials reported in this work are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H and N). EPR spectra were obtained at X-band frequencies on a Varian E-109C spectrometer. Spectra at 77 K were collected using a quartz dewar. The calibrant was DPPH ($g = 2.0037$). Magnetic susceptibility was measured using a PM 155 vibrating-sample magnetometer fitted with a Walker Scientific L75 FBAL magnet.

Synthesis of ligands:

The ligands H_2L^1 and H_2L^2 have been synthesized from the reported procedure²⁷.

Synthesis of the complexes:

Synthesis of $[\text{VO}_2(\text{HL})]$ complexes:

These complexes were prepared by the same general procedure based on the reaction of $[\text{VO}(\text{acac})_2]$ with H_2L in acetone in presence of water. Details are given below for a representative case.

$[VO_2(HL^1)] :$

To a solution of (30 cm³) of $[VO(acac)_2]$ (0.200 g, 0.75 mmol) in acetone was added H_2L^1 (0.180 g, 0.75 mmol) dissolving in acetone (20 cm³) and the mixture was stirred for 1 h. After 1 h, 1 cm³ of water was added and stirring was continued for 4 h. The yellow precipitated that appeared was filtered off, washed thoroughly with acetone and dried *in vacuo*, yield 70% (Found : C, 52.12; H, 3.49; N, 8.74. Calcd. for $C_{14}H_{11}N_2O_4V$: C, 52.19; H, 3.44; N, 8.69%); IR (KBr, ν , cm⁻¹) 990 (V=O), 975 (V=O), 1620 (C=N), 3360 (N-H), 1698 (C=O); UV-vis [DMSO, λ_{max} , nm (ϵ , dm³ mol⁻¹ cm⁻¹)] 400 (13200), 325 (17800); $VO_2^+ - VO_2$ couple : $E_{1/2}$ (vs SCE, DMSO, scan rate, 50 mV s⁻¹) 0.45 V (E_p = 200 mV); ¹H NMR (300 MHz, DMSO-*d*₆, 298 K, δ) 9.00 (1H, s, N(2)-H, disappears on shaking with D₂O), 8.90 (1H, s, CH=N) and 8.00–6.80 (9H, m, aromatic protons); ⁵¹V (DMSO-*d*₆, δ) –583.

$[VO_2(HL^2)] :$

Yield 64% (Found : C, 58.02; H, 3.48; N, 7.57. Calcd. for $C_{18}H_{13}N_2O_4V$: C, 58.08; H, 3.52; N, 7.52%); IR (KBr, ν , cm⁻¹) 995 (V=O), 970 (V=O), 1600 (C=N), 3380 (N-H), 1702 (C=O); UV-vis [DMSO, λ_{max} , nm (ϵ , dm³ mol⁻¹ cm⁻¹)] 435 (8200), 330 (7950); $VO_2^+ - VO_2$ couple : $E_{1/2}$ (vs SCE, DMSO, scan rate, 50 mV s⁻¹) 0.32 V (E_p = 180 mV); ¹H NMR (300 MHz, DMSO-*d*₆, 298 K, δ) 9.78 (1H, s, N(2)-H, disappears on shaking with D₂O), 9.70 (1H, s, CH=N) and 8.53–7.00 (11H, m, aromatic protons); ⁵¹V (DMSO-*d*₆, δ) –571.

Synthesis of $[V_2O_3(L^2)_2]$ complexes :

$[V_2O_3(L^2)_2]$ was prepared by the following procedure. The details are given below as illustrative.

$[V_2O_3(L^2)_2] :$

To a solution of $[VO(acac)_2]$ (200 mg, 0.75 mmol) in 25 cm³ of acetone was added 180 mg (0.75 mmol) of H_2L^2 . The resulting mixture was refluxed for half an hour and left to evaporate at room temperature in air. The dark coloured crystalline solid that was deposited, filtered off and washed with water and dried over P_4O_{10} *in vacuo*, yield 81% (Found : C, 59.57; H, 3.30; N, 7.67. Calcd. for $C_{36}H_{24}N_4O_7V_2$: C, 59.52; H, 3.33; N, 7.71%); IR (KBr, ν , cm⁻¹) 980 (V=O), 770 (V–O–V), 1605 (C=N); UV-vis [CH_2Cl_2 , λ_{max} , nm (ϵ , dm³ mol⁻¹ cm⁻¹)] 470 (6100), 320 (6700); $V_2O_3^{4+} - V_2O_3^{3+}$ couple $E_{1/2}$ (vs SCE, CH_2Cl_2 , scan rate 50 mV s⁻¹) 0.27 V (E_p

= 70 mV); ¹H NMR (300 MHz, $CDCl_3$ -*d*₆, 298 K, δ) 9.78 (1H, s, CH=N) and 8.53–7.11 (17H, m, aromatic protons).

Synthesis of $Et_4N[V_2O_3(L^2)_2]$ complexes :

$Et_4N[V_2O_3(L^2)_2]$ was prepared by the following procedure. The details are given below as illustrative.

$Et_4N[V_2O_3(L^2)_2] :$

A solution of 100 mg (0.16 mmol) of $[V_2O_3(L^2)_2]$ and 36 mg of TEAP in 30 cm³ of dry dichloromethane was reduced coulometrically at a constant potential of 0.0 V vs SCE in nitrogen atmosphere. As the reduction proceeded the brown coloured solution gradually changes to green. After complete reduction the resulting green solution was evaporated under reduced pressure and a green mass was obtained, yield 93% (Found : C, 61.62; H, 5.21; N, 8.12. Calcd. for $C_{44}H_{44}N_5O_7V_2$: C, 61.69; H, 5.18; N, 8.17%); IR (KBr, ν , cm⁻¹) 980 (V=O), 775 (V–O–V), 1610 (C=N); UV-vis [CH_2Cl_2 , λ_{max} , nm (ϵ , dm³ mol⁻¹ cm⁻¹)] 950 (190), 490 (8200), 345 (5200); $V_2O_3^{3+} - V_2O_3^{4+}$ couple : $E_{1/2}$ = 0.27 V (E_p = 80 mV); μ_{eff} = 1.77 μ_B .

X-Ray crystallography :

Bright yellow single crystals of $[V^VO_2(HL^1)]$ ($0.4 \times 0.3 \times 0.2$ mm³) and were grown by slow evaporation from methanol solution at room temperature. Cell parameters were determined by least-squares fit of 30 machine-centered reflections (2θ range 15–30°). Data were collected by the ω -scan technique in the 2θ range 3–50° on a Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). Two check reflections measured after every 198 reflections showed no intensity reduction. All data were corrected for Lorentz-polarisation effects and empirical absorption correction was performed on the basis of azimuthal scan of six reflections for the crystal⁴³.

All calculations for data reduction, structure solution and refinement were done using the programs of SHEXTL-version 5.03⁴⁴. The structure was solved by direct method and was refined by full-matrix least square on F^2 . Total collected reflections for $[V^VO_2(HL^1)]$ were 2547 of which 2350 were unique and 1891 satisfying $I > 2.0\sigma(I)$ were used for structure solution. All nonhydrogen were refined anisotropically and the crucial hydrogen atoms were directly located in difference Fourier maps and were refined isotropically. The remaining hydrogen atoms were

Table 4. Crystal data for the complex [VO₂(HL¹)]

Complex	VO ₂ (HL ¹)
Empirical formula	C ₁₄ H ₁₁ N ₂ O ₄ V
Formula weight	322.19
Crystal system	Monoclinic
Space group	P2 ₁ /c
a (Å)	14.165(7)
b (Å)	8.120(4)
c (Å)	11.779(6)
β (°)	100.98(4)
V (Å ³)	1333.0(11)
Z	4
ρ _{calc} (mg m ⁻³)	1.609
μ/mm ⁻¹	0.763
Total reflections	2547
Independent reflection (R _{int})	2350 (0.0272)
R ^a , wR ² ^b [I > 2σ(I)]	0.0346, 0.0891
Goodness of fit on F ²	1.057
^a R1 = Σ F _o - F _c / Σ F _o .	
^b wR2 = [Σ{w(F _o ² - F _c ²) ² } / Σ{w(F _o ²) ² }] ^{1/2} .	

included in calculated position (Riding model). Significant crystal data are listed in Table 4.

Supplementary material :

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 207762 for [VO₂(HL¹)]. Copies may be obtained free of charge from : The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax : +44-1223-336033; E-mail : deposit@ccdc.cam.ac.uk or www.http://www.ccdc.cam.ac.uk).

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