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SYNTHESIS AND CHARACTERIZATION OF [*N*,*N*′-ETHYLENEBIS(3-ETHOXYSALICYLIDENEAMINATO)] OXOVANADIUM(IV)

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Abstract—The synthesis, spectra and X-ray crystal structure of [$V^{IV}O$(3-EtOsalen)] [where 3-EtOsalen is the Schiff base *N*,*N*′-ethylenebis(3-ethoxysalicylideneaminate)] are reported. The Gaussian analysis of the visible spectrum of the complex in acetonitrile yielded four peaks, at 12,570, 15,190, 17,010 and 20,710 cm^{-1}, assigned as the four *d–d* transitions. In the IR spectra of three samples synthesized in different solvents, two sharp bands appeared at 3524 and 3577 cm^{-1}. These are assigned as O—H stretching frequencies of the water of crystallization strongly hydrogen bonded to two independent pairs of ligand oxygen atoms. The molecule adopts the square-pyramidal geometry characteristic of oxovanadium(IV) chelates.

The most important vanadium(IV) compounds are those containing the oxovanadium(IV) VO^{2+} unit and numerous complexes of this ion have been prepared and studied. The majority of complexes containing the VO^{2+} unit are deep blue or green[1,2] and have a strong V═O stretching band in the IR[2–5] in the range 910–1010 cm^{-1}. Oxovanadium compounds may, depending on the nature of the ligands, be cationic, neutral or anionic and be either five-coordinate, where the stereochemistry is that of a square pyramid, or six-coordinate, containing a distorted octahedron.[2–4,6,7]

There have been a considerable number of spectroscopic studies on oxovanadium(IV) complexes.[2–4,7–14] The vanadium valence shell electronic structure is d^1 and the crystal field is dominated by the strong V═O interaction. Normally, the experimental data are not easily interpreted. One possible reason for the lack of self-consistency is that the three-dimensional local geometry around the vanadium may change from complex to complex. We have prepared and characterized several oxovanadium(IV) complexes of tetradentate Schiff base ligands.[15–17] Here we report the preparation and characterization of the oxovanadium(IV) complex of the tetradentate Schiff base ligand *N*,*N*′-ethylenebis(3-ethoxysalicylideneaminate) (3-EtOsalen).

EXPERIMENTAL

Materials

Ethylenediamine, 3-ethoxysalicylaldehyde and deuterium oxide (D_2O 99.9 atom% deuterium) were purchased from Aldrich Chemical Company and used as-received. Vanadium(IV) sulphate oxide

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(Alfa Morton Thiokol, Inc.) was used as-received. Methanol was purified and dried as described previously.[18] All other solvents and reagents were obtained commercially and used without further purification.

Synthesis of compounds

Analyses were made by the microanalytical laboratories of the Universidade de São Paulo, São Paulo, São Paulo and the Universidade Estadual de Campinas, Campinas, São Paulo, Brazil. In general, no precautions were taken to exclude air from the reaction system. The oxovanadium(IV) complex was stable in air.

Preparation of N,N′-*ethylenebis*(3-*ethoxysalicylideneaminate*)

To a hot solution of 9.991 g (60 mmol) of 3-ethoxysalicylaldehyde, 2.08 cm^3 (31 mmol) of ethylenediamine was added. After stirring and heating at 80°C for 2 h, the resulting solution, a yellow crystalline solid, was obtained. The ligand was used without further purification. Yield 9.622 g, 90%; m.p. 139–140°C. Found: C, 67.3; H, 6.7; N, 7.9. Calc. for $C_{20}H_{24}O_4N_2$: C, 67.4; H, 6.8; N, 7.9.

Preparation of [V^{IV}O(3-EtOsalen)]

A solution of oxovanadium(IV) sulphate (1.159 g, 5 mmol) in 20 cm^3 of distilled water was added to a hot methanol solution containing 1.782 g (5 mmol) of the Schiff base ligand and 1.497 g (11 mmol) of sodium acetate trihydrate. Although a green precipitate formed almost immediately, the mixture was refluxed with stirring for 4 h. After cooling slowly to room temperature, the reaction mixture was held at 0°C for 12 h. The resulting precipitate was collected by filtration, washed twice with 20 cm^3 of distilled water and twice with 10 cm^3 of methanol and dried over silica in a desiccator *in vacuo* at room temperature for 72 h. The complex was recrystallized from acetonitrile. Yield 2.153 g, 98%; m.p. 266–268°C. Found: C, 54.6; H, 5.5; N, 6.4; V, 11.5. Calc. for $VC_{20}H_{22}O_5N_2 \cdot H_2O$: C, 54.7; H, 5.5; N, 6.4; V, 11.6%.

Two variations of this synthesis were tried. The same proportions of the ligand, sodium acetate trihydrate and oxovanadium(IV) sulphate were used. The rest of the procedure was identical to the methanol–water synthesis.

In the first, acetone was used in place of methanol as the solvent for the ligand. Yield 2.135 g, 97%; m.p. 267–268°C. Found: C, 54.6; H, 5.5; N, 6.5; V, 11.6%.

In the second, the ligand was dissolved in dried purified methanol and deuterium oxide instead of water was used for the oxovanadium(IV) sulphate solution. Yield 2.095 g, 95%; m.p. 266–269°C. Found: C, 54.7; H, 5.5; N, 6.4; V, 11.5%.

Spectral studies

IR spectra of the free ligand and the complexes were recorded in the 200–4000 cm^{-1} range as pressed discs (1% by weight in KBr) with a Bomem Michelson 102 FT IR spectrophotometer. Electronic spectra were recorded in the 250–850 nm range using a Cary Model 219. The visible spectra of the acetonitrile solutions at 25.0 ± 0.1°C were obtained using matched 0.010-, 1.000- or 10.000-cm quartz cells. The spectra were resolved by Gaussian analysis with FORTRAN programs adapted[19] from Jones *et al.*[20]

X-ray diffraction determination

The recrystallization of the [V^{IV}O(3-EtOsalen)] complex from acetonitrile yielded dark green crystals, whose structure was determined. A complete data set was collected on an Enraf–Nonius CAD-4 four-circle diffractometer with monochromatic Mo-K_α ($\gamma = 0.71073$ Å) radiation at room temperature. Experimental details are included in Table 1. Cell dimensions and the orientation matrices were calculated by least-squares refinement from 25 centred reflections. Diffraction intensities were measured by the ω–2θ scan technique using a variable scan speed between 6.7 and 20.0° min^{-1} determined by a pre-scan at 20.0° min^{-1}. The intensity of one standard reflection was essentially constant over the duration of the experiments. Data were corrected for Lorentz polarization and absorption effects following the procedure of Walker and Stuart[21]. The structure determination and refinement were performed with the SHELX76[22] system of programs. Bonded hydrogen-atom scattering factors[23] and complex scattering factors[24,25] for the remaining atoms were employed. The molecular drawing (Fig. 1) was produced with the program ORTEP.[26]

The structure was solved by standard Patterson and difference Fourier techniques and refined by full-matrix least-squares methods with anisotropic thermal parameters for the non-hydrogen atoms. All non-water hydrogen atoms were located from difference Fourier maps and included as fixed contributors with one refined common isotropic temperature factor of 6.6(1) Å^2. A difference map at this stage unequivocally showed four hydrogen sites around the water molecule, which were interpreted as two equally occupied orientations for the water

Table 1. Crystal data, data collection details and structure refinement results for $VC_{20}H_{22}O_5N_2 \cdot H_2O$

Chemical formula	$VC_{20}H_{22}O_5N_2 \cdot H_2O$
Molecular weight	439.36
Space group	$P2_1/c$
Lattice parameters	
a	9.423(1) Å
b	17.005(4) Å
c	12.773(2) Å
β	98.23(1)°
V	2026(1) $Å^3$
Z	4
D_{calc}	1.441 g cm^{-3}
Sample dimensions	0.22 × 0.33 × 0.50 mm
Radiation	Mo-K_α, $\gamma = 0.71073$ Å
Temperature	25°C
Linear absorption coefficient, μ	4.77 cm^{-1}
Transmission factors (max, min)	1.12, 0.865
Scan technique	ω–2θ
Scan speed range	6.7–20° min^{-1}
θ range for data collection	0–25°
$F(000)$	916
Number of independent reflections	3256
Number of reflections above $3\sigma(I)$	2566
Number of refined parameters	264
Minimized function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$w = [\sigma^2(\lvert F_o\rvert) + 0.001\lvert F_o\rvert^2]^{-1}$
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.039
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.042
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(M-N)]^{1/2}$	1.46
$h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}$	−11, 11; 0, 20; 0, 15
Maximum, minimum residual electron density, ρ	0.23, −0.29 e $Å^{-3}$

molecule in the crystal. The water hydrogens found were also included as fixed contributors with a refined overall temperature factor of 9(1) $Å^2$. A list comparing observed and calculated structure factors is available as supplementary material.

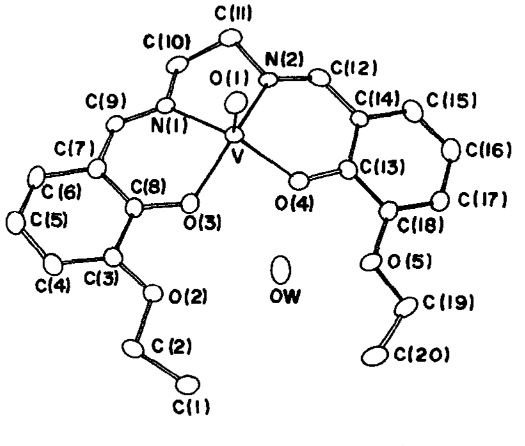

Fig. 1. Molecular structure and numbering scheme of $[V^{IV}O(3\text{-EtOsalen})]$.

RESULTS AND DISCUSSION

Oxovanadium(IV) complexes of tetradentate Schiff base ligands were synthesized by the same general procedure[15–17] according to:

$$\text{Schiff base} + 2\text{NaOAc} \rightarrow (\text{Schiff base})^{2-} + 2\text{HOAc} + 2\text{Na}^+$$

$$\text{VO}^{2+} + (\text{Schiff base})^{2-} \rightarrow [\text{V}^{IV}\text{O(Schiff base)}]\downarrow$$

Three solvent systems were used for the synthesis: methanol, acetone, dry methanol for the Schiff base, 3-EtOsalen, and water, water, deuterium oxide for vanadium(IV) sulphate oxide, respectively. The three products displayed properties identical within experimental errors. The yields were comparable (95–98%). The complexes are stable in air, both in solution and in the crystalline state. The green powder was recrystallized from acetonitrile, yielding dark green crystals whose structure was determined.

The IR spectra (Fig. 2) of the free ligand and the complex present various bands in the region 200–400 cm^{-1}. The O—H stretching frequency of the free ligand is expected in the region 3300–3800 cm^{-1}. However, the O—H stretching frequency is displaced to around 2583 cm^{-1} due to the internal hydrogen bridge OH---N=C.[27,28] The C=N stretching frequency at 1632 cm^{-1} is in the region 1590–1640 cm^{-1} reported for similar ligands.[4,27–31] The C—N stretching frequency is reported[30,32,33] in the region 1350–1410 cm^{-1}. For the free ligand, the medium band at 1390 cm^{-1} is assigned to the C—N stretching frequency. A fourth characteristic band due to the C—O stretching frequency appears as a weak band at 1292 cm^{-1}, within the range 1290–1340 cm^{-1} reported for similar ligands.[27,28,31–33]

The characteristic V=O stretching frequency in the oxovanadium(IV) complex appears as a medium strong band at 979 cm^{-1}, within the range 970–997 cm^{-1} reported for similar oxovanadium(IV) complexes.[2–5,14,33–35] The weak O—H stretching frequency of the free ligand at 2580 cm^{-1} is absent, as expected, in the spectrum of the coordinated ligand, reinforcing the assignment to a hydrogen bridge. On coordination of the Schiff base ligand, the C—N and C—O stretching frequencies are slightly displaced to higher frequencies, 1394 and 1300 cm^{-1}, respectively. The C=N stretching frequency is displaced to lower frequency, 1616 cm^{-1}, indicating a decrease in the C=N bond order due to the coordinate bond of the metal with the azomethine nitrogen lone pair.[4,10,12,30,34,35] The far-IR indicates that M—O and M—N absorption would occur at 303 cm^{-1} and 552 and 406 cm^{-1}, respectively, as reported.[10,12,15,30,33] These bands are observed as new absorption peaks of the complex that are not present in the spectrum of the free ligand. A preliminary band fit analysis of the spectra in the regions of interest was performed. These data are presented in Table 2.

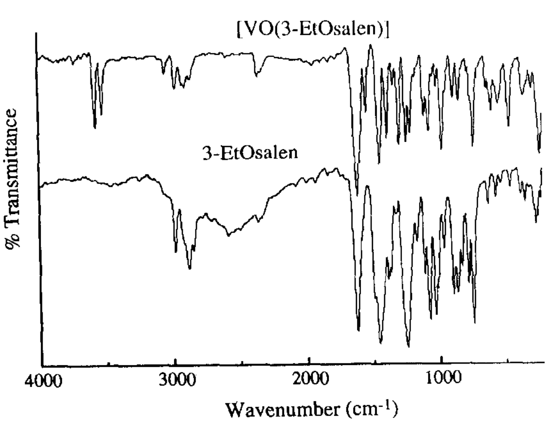

Fig. 2. IR spectra (200–400 cm^{-1}) of 3-EtOsalen and [V^{IV}O(3-EtOsalen)].

A significant difference is observed in the oxovanadium(IV) complex spectrum in comparison to the free ligand spectrum; two sharp bands appear at 3524 and 3577 cm^{-1}. A preliminary band fit analysis gives bands at 3526.5 and 3578 cm^{-1}. Strong bands in this region may arise from primary alcohols and primary amines, i.e. O—H and N—H stretches.[36] The complex synthesized in acetone–water also presents these two bands with the same intensities at identical positions. The substitution of deuterium for hydrogen should cause a shift to lower frequencies of about 100 cm^{-1}; therefore the solvent system, dry methanol and deuterium oxide, 99.9 atom% deuterium, was used. As with the acetone–water solvent system, there was no alteration of frequency or intensity for either band. The waters of hydration of the sodium acetate and vanadium(IV) sulphate, as well as the exchange of deuterium for the —OH proton of methanol, may result in a considerable concentration of H_2O in the system. These two bands remain unaltered even after drying the complex over P_4O_{10} *in vacuo* at 80°C for 8 h. On the basis of the single-crystal X-ray diffraction study (discussed in further detail below), these bands are assigned as O—H stretching frequencies of the water of crystallization attached by strong hydrogen bonds to the four oxygens of the coordinated ligand. The thermal decomposition[16] of this complex occurs in three steps. The first mass loss occurs up to about 115°C and is attributed to

Table 2. IR spectral data (cm^{-1})

EtOsalen	[V^{IV}O(EtOsalen)]	Tentative assignments
2583w[a]		ν(O—H--N=C)
(2587.8)[b]		
1632s	1616	ν(C=N)
(1629.2)	(1619.1)	
1390m	1394m	ν(C—N)
(1388.1)	(1394.9)	
1292w	1300w	ν(C—O)
(1289.6)	(1301.7)	
	979ms	ν(V=O)
	(980.0)	
	552m	ν(V—N)
	(555.9)	
	406w	ν(V—N)
	(404.8)	
	303wm	ν(V—O)
	(304.0)	

[a] w, weak; s, strong; m, medium; ms, medium strong; wm, weak-medium.

[b] Values from band fit analysis.

the loss of the hydration water. The second mass loss occurs between 240 and 260°C, and is due to the loss of the coordinated water, hydrogen bonded to the oxygens of the ligand, and CH_3CN from the 3-EtOsalen ligand.

Similar bands are also observed at 3512 and 3563 cm^{-1} for the corresponding copper(II) complex.[37] The IR spectra of the oxovanadium(IV)[15] and copper(II)[37] complexes of the Schiff base, *N,N′-trans*-1,2-cyclohexylenebis(3-ethoxysalicylideneaminate), present two sharp bands at 3525 and 3582 cm^{-1} and 3499 and 3544 cm^{-1}, respectively. These bands are observed at 3521 and 3578 cm^{-1} for the oxovanadium(IV) complex of *N,N*-1,2-propylenebis(3-ethoxysalicylideneaminate).[15]

The Gaussian analysis of the visible portion (11,760–25,000 cm^{-1}) of the optical absorption spectrum in acetonitrile yields four peaks at 12,570, 15,190, 17,010 and 20,710 cm^{-1}. The Gaussian analysis of the electronic spectrum in the visible region is given in Fig. 3. The calculated values for the absorption maximum,[19,20] the molar absorptivity[19,20] and the oscillator strength[38] for each peak are given in Table 3.

We propose the energy order for the *d* orbitals of $[V^{IV}O(3\text{-EtOsalen})]$ as: $xy < yz < xz < x^2-y^2 < z^2$ on the basis of the theoretical studies by Vanquickenborne and McGlynn[39] and Kuska and Yang.[40] The xz and yz orbitals can be inverted depending only on the choice of the coordinates for the stronger ligand field.[41] The complex has a low symmetry, approximately C_s, which results in xz, yz splitting, causing the $xy \rightarrow xz$ and $xy \rightarrow yz$ transitions. The inversion of the $xy \rightarrow xz$, $xy \rightarrow yz$ transitions with the $xy \rightarrow x^2-y^2$ transition agrees with previous reports.[6,9,39–41]

The most consistent assignment for the bands is to assign the 12,570 and 15,190 cm^{-1} bands as the split $xy \rightarrow xz$, yz transitions, the 17,010 cm^{-1} band as the $xy \rightarrow x^2-y^2$ transition and the 20,710 cm^{-1} band as the $xy \rightarrow z^2$ transition. Kuska and Yang[8] have also observed the large splitting of the xz, yz levels. Extended Hückel calculations on C_{2v} distorted square pyramidal geometry oxovanadium(IV) complexes[40,41] resulted in an xz, yz splitting of about 2000 cm^{-1}.

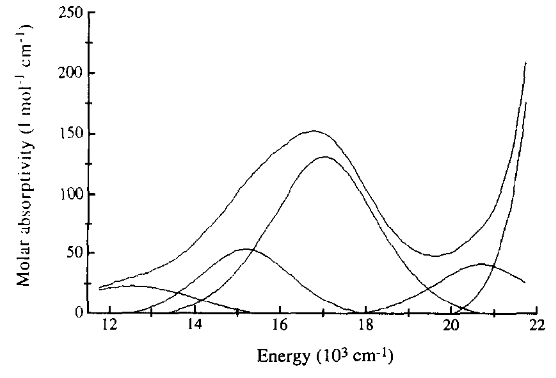

Fig. 3. Gaussian analysis of $[V^{IV}O(3\text{-EtOsalen})]$ for the acetonitrile electronic spectrum.

Table 3. Electronic spectrum of $[V^{IV}O(3\text{-EtOsalen})]$ in acetonitrile

Peak	ν_{max} ($cm^{-1} \times 10^3$)	ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	Oscillator strength
1	12.57 ± 0.03^a	28.5 ± 0.2	$(4.78 \pm 0.05) \times 10^{-4}$
2	15.19 ± 0.01	59.0 ± 0.9	$(7.13 \pm 0.19) \times 10^{-4}$
3	17.01 ± 0.01	136.4 ± 0.3	$(1.86 \pm 0.01) \times 10^{-3}$
4	20.71 ± 0.04	47.0 ± 0.3	$(6.00 \pm 0.33) \times 10^{-4}$

[a] Standard deviation.

The interatomic bond distances are given in Table 4 and the interbond angles in Table 5. Fractional coordinates and equivalent isotropic temperature factors for all non-hydrogen atoms are provided as supplementary material.

Figure 1 is a drawing of the complex showing the labelling of all non-hydrogen atoms and their thermal vibration ellipsoids. The parameters of these ellipsoids, along with the hydrogen atoms' atomic coordinates and temperature factors, are provided as supplementary material. The coordination around the vanadium atom is in the form of a square pyramid, with the base formed by two nitrogen and two oxygen atoms of the Schiff base ligand, and the vanadyl oxygen at the apical

Table 4. Interatomic bond distances (Å) for the $VC_{20}H_{22}O_5N_2 \cdot H_2O$ complex

V—O(1)	1.590(2)	C(3)—C(4)	1.374(5)
V—O(3)	1.921(2)	C(3)—C(8)	1.417(4)
V—O(4)	1.938(2)	C(4)—C(5)	1.396(5)
V—N(1)	2.060(2)	C(5)—C(6)	1.357(5)
V—N(2)	2.060(3)	C(6)—C(7)	1.414(5)
O(2)—C(2)	1.427(4)	C(7)—C(8)	1.412(4)
O(2)—C(3)	1.366(4)	C(7)—C(9)	1.434(4)
O(3)—C(8)	1.322(4)	C(10)—C(11)	1.518(5)
O(4)—C(13)	1.320(4)	C(12)—C(14)	1.440(5)
O(5)—C(18)	1.362(4)	C(13)—C(14)	1.409(4)
O(5)—C(19)	1.442(4)	C(13)—C(18)	1.418(4)
N(1)—C(9)	1.282(5)	C(14)—C(15)	1.416(4)
N(1)—C(10)	1.479(5)	C(15)—C(16)	1.354(5)
N(2)—C(11)	1.483(4)	C(16)—C(17)	1.395(5)
N(2)—C(12)	1.296(5)	C(17)—C(18)	1.385(5)
C(1)—C(2)	1.490(5)	C(19)—C(20)	1.503(6)

Table 5. Selected bond angles (°) for the $VC_{20}H_{22}O_5N_2 \cdot H_2O$ complex

O(1)—V—O(3)	112.8(1)	C(3)—C(4)—C(5)	119.9(3)
O(1)—V—O(4)	107.4(1)	C(4)—C(5)—C(6)	120.8(3)
O(1)—V—N(1)	102.2(1)	C(5)—C(6)—C(7)	120.5(3)
O(1)—V—N(2)	108.6(1)	C(6)—C(7)—C(8)	119.6(3)
O(3)—V—O(4)	87.39(9)	C(6)—C(7)—C(9)	118.2(3)
O(3)—V—N(1)	86.59(9)	C(8)—C(7)—C(9)	121.9(3)
O(3)—V—N(2)	138.0(1)	O(3)—C(8)—C(3)	117.3(3)
O(4)—V—N(1)	149.8(1)	O(3)—C(8)—C(7)	124.1(3)
O(4)—V—N(2)	86.3(1)	C(3)—C(8)—C(7)	118.1(3)
N(1)—V—N(2)	78.7(1)	N(1)—C(9)—C(7)	124.5(3)
V—O(3)—C(8)	131.1(2)	N(1)—C(10)—C(11)	106.8(3)
V—O(4)—C(13)	127.0(2)	N(2)—C(11)—C(10)	107.4(3)
V—N(1)—C(9)	128.1(2)	N(2)—C(12)—C(14)	124.7(3)
V—N(1)—C(10)	111.4(2)	O(4)—C(13)—C(14)	123.5(3)
V—N(2)—C(11)	116.0(2)	O(4)—C(13)—C(18)	118.3(3)
V—N(2)—C(12)	126.0(2)	C(14)—C(13)—C(18)	118.1(3)
C(2)—O(2)—C(3)	118.8(3)	C(12)—C(14)—C(13)	121.4(3)
C(18)—O(5)—C(19)	117.5(2)	C(12)—C(14)—C(15)	119.0(3)
C(9)—N(1)—C(10)	120.3(3)	C(13)—C(14)—C(15)	119.5(3)
C(11)—N(2)—C(12)	118.0(3)	C(14)—C(15)—C(16)	121.0(3)
O(2)—C(2)—C(1)	107.1(3)	C(15)—C(16)—C(17)	120.5(3)
O(2)—C(3)—C(4)	125.1(3)	C(16)—C(17)—C(18)	120.0(3)
O(2)—C(3)—C(8)	114.0(3)	O(5)—C(18)—C(13)	114.3(3)
C(4)—C(3)—C(8)	120.9(3)	O(5)—C(18)—C(17)	124.9(3)
C(3)—C(4)—C(5)	119.9(3)	C(13)—C(18)—C(17)	120.8(3)
		O(5)—C(19)—C(20)	107.0(3)

position. The vanadium atom is 0.610 Å above the least-squares plane of the coordination pyramid base (Table 6). Comparisons are made with appropriate bond lengths and angles in [V^{IV}O(salen)] and [V^{IV}O(tsalen)], where salen is the Schiff base *N*,*N*′-ethylenebis(salicylideneaminate) and tsalen is *N*,*N*′-ethylenebis(thiosalicylideneaminate) (Table 7). A crystallization water molecule, strongly hydrogen bonded to the two independent pairs of ligand atoms (Table 8), completes the structure and

Table 6. Least-squares plane through the ligands of the vanadium atom; the plane equation is of the form $A^*x+B^*y+c^*z-D = 0$, where A, B, C and D are constants and x, y and z are the atomic orthogonalized coordinates

	A	*B*	*C*	*D*	
	0.5652	0.6396	−0.5210	3.2035	
Atom	*x*	*y*	*z*	Distance	E.s.d.
O(3)	7.2452	2.2871	4.7034	−0.096	0.002
O(4)	9.2292	0.5424	4.3445	0.096	0.002
N(1)	8.4682	3.3159	6.9193	0.098	0.002
N(2)	10.1936	1.3621	6.7701	−0.098	0.003
Other atoms (out of plane)					
V	9.0788	2.2361	5.2748	0.610	0.001
O(1)	9.9946	3.2836	4.5050	2.198	0.002
OW	7.6598	1.3349	1.8998	0.990	0.003

Chi squared = 7348.1.

Table 7. Comparison of selected bond distances (Å) and angles (°)

	[$V^{IV}O$(EtOsalen)]	[$V^{IV}O$(salen)][a]	[$V^{IV}O$(tsalen)][a]
V═O	1.590(2)	1.590(1)	1.590(6)
V—O(ave)	1.930	1.921	
V—S(ave)			2.346
V—N(ave)	2.060	2.050	2.080
V—plane[b]	0.610(2)	0.609	0.608(1)
N—V—N	78.7(1)	78.45(5)	79.9(2)
O—V—N(ave)	86.4	89.2	
S—V—N(ave)			89.1

[a] Ref. 14.

[b] Distances of vanadium from best plane of "in-plane" donors.

Table 8. Relevant interatomic distances (Å) and angles (°) involved in hydrogen bonding

O(2)—OW	3.034(4)
O(3)—OW	2.990(4)
O(4)—OW	3.011(4)
O(5)—OW	2.977(4)
O(2)—H(1′)(OW)	2.159(2)
O(3)—H(2)(OW)	2.114(3)
O(4)—H(1)(OW)	2.312(2)
O(5)—H(2′)(OW)	2.002(2)
OW—H(1)(OW)	0.891(3)
OW—H(2)(OW)	0.918(3)
OW—H(1′)(OW)	0.939(3)
OW—H(2′)(OW)	0.984(3)
H(1)O(W)—OW—H(1′)(OW)	113.8(3)
H(2)(OW)—OW—H(2′)(OW)	110.6(3)
O(2)—H(1′)(OW)—OW	154.2(2)
O(3)—H(2)(OW)—OW	159.4(2)
O(4)—H(1)(OW)—OW	135.3(2)
O(5)—H(2′)(OW)—OW	170.2(2)

causes the strong sharp bands at 3524 and 3577 cm^{-1} in the IR spectrum.

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