Oxovanadium(IV) complexes with aromatic aldehydes

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Abstract

The synthesis, structure and spectroscopic properties of complexes with the formula $[V^{IV}O(dsal)_2(H_2O)]$, where Hdsal = salicylaldehyde, *o*-vanillin and 3-ethoxysalicylaldehyde, are presented. The crystal and molecular structures of $[V^{IV}O(o\text{-van})_2(H_2O)]$ (**1**) (*o*-Hvan = *o*-vanillin = 3-methoxysalicylaldehyde) is studied by single-crystal X-ray diffraction. Each molecule exhibits an octahedral geometry with the two *o*-van ligands coordinated *cis* to the $V^{IV}O^{2+}$ group. **1** is the first example of a structurally characterized vanadium complex involving $O_{aldehyde}$ as the donor atom and this enables a comparison between the bonding characteristics and the contributions of $O_{aldehyde}$, O_{amide}, $O_{carboxylate}$ and O_{ketone} (in acetylacetone) to the parallel hyperfine coupling constant in VOL_2 complexes. ©2000 Elsevier Science Inc. All rights reserved.

Keywords: Oxovanadium(IV) complexes; Salicylaldehyde; *o*-Vanillin; Electron paramagnetic resonance spectra

1. Introduction

One of the most important physiological responses of vanadium is its insulin-mimetic property [1–4]. In addition, the oxovanadium(IV) cation can be used as a spectroscopic probe of divalent metal sites in enzymes. ESR spectroscopy has been used frequently for this purpose providing information regarding the vanadium donors' identity through the use of the additivity rule for ^{51}V parallel hyperfine coupling constants established by Chasteen [5] and expanded by others [6–12]. Recently, there has been great interest in characterizing the coordination environment of V(IV) and V(V) in vanadium-peptide complexes, particularly the possible formation of bonds involving N_{amide} or O_{amide} [7–19] and in evaluating the contributions of these donors for use in the additivity relationship.

To date, there are only a few well-characterized vanadium-dipeptide complexes [9–12], and the interaction of vanadium with deprotonated N_{amide} is well established. There also exist a few solution studies [7,8,12,15–19] and structurally characterized examples [8,12,14,18,19] pinpointing the interaction of vanadium with the carbonyl oxygen of the –NHCO– functionality: $[V^VOCl_3(Hpycan)]$ [18], $[V^{IV}OCl_2(CH_3CN)(Hpycan)]$ [18] (Hpycan = *N*-(2-nitrophenyl)pyridine-2-carboxamide), $[V^VOCl_2(OC_2H_5)(Hpheca)]$ [12]

(Hpheca = *N*-(phenyl)pyridine-2-carboxamide), $[V^{IV}O(ada)(H_2O)]$ ($H_2ada = N$-(carbamoylmethyl)-iminodiacetic acid) [8], and $[V^VO(NH_2O)_2(GlyGly)]$ [14]. In all structurally characterized complexes, except for $[V^{IV}O(ada)(H_2O)]$, the coordination of the carbonyl oxygen is axial.

Herein, we describe the synthesis and characterization by single-crystal X-ray diffraction of $[V^{IV}O(o\text{-van})_2(H_2O)]$ (**1**) (*o*-Hvan = *o*-vanillin = 3-methoxysalicylaldehyde), as well as the preparation of $[V^{IV}O(Etsal)_2(H_2O)]$ (**2**) (*o*-Etsal = 3-ethoxysalicylaldehyde) and of $[V^{IV}O(sal)_2(H_2O)]$ (**3**) (Hsal = salicylaldehyde). To our knowledge, **1** is the first example of a structurally characterized vanadium complex involving an aldehyde carbonyl oxygen ($O_{aldehyde}$) as a donor atom, and the second example of an oxovanadium(IV/V) complex involving an equatorially coordinated carbonyl oxygen. This enables comparison between the bonding characteristics of $O_{aldehyde}$, O_{amide}, $O_{carboxylate}$ and O_{ketone} (O_{ketone} in 1,3-butanedionato complexes).

2. Experimental

2.1. Chemicals and instrumentation

All reactions were carried out in nitrogen atmosphere using standard inert-atmosphere techniques. Solvents were

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degassed and used without further purification. Salicylaldehyde, *o*-vanillin and 3-ethoxysalicylaldehyde were purchased from Sigma and $VOCl_2$ from Carlo Erba; vanadyl sulfate and all other reagents used are from Merck.

ESR spectra were recorded at 77 K (on glasses made by freezing solutions in liquid nitrogen) on a Bruker ESR-ER 200D X-band spectrometer. Visible spectra and infrared spectra were recorded on a Perkin-Elmer Lambda 9 or a Mattson 1000 FT-IR spectrometer, respectively. Elemental analyses were performed by Laboratório de Análises, IST, Lisbon, Portugal.

The compounds were prepared by two similar methods. One was previously reported [20] and includes the use of $VOCl_2$ and sodium acetate. In the second method $VOSO_4$ and NaOH were used instead of $VOCl_2$ and sodium acetate, respectively. The compounds precipitated within minutes of neutralization with base and were washed with water, ethanol/water (50/50) and diethyl ether.

2.2. Synthesis

$[VO(o\text{-van})_2(H_2O)]$ (**1**): To a solution of 0.228 g of *o*-vanillin (1.5 mmol) in 10 mL of methanol 3 mL of a solution of 0.132 mg (0.5 mmol) of $VOSO_4$ were added dropwise. Pyridine was added till pH 5. Four days later crystals of **1** were separated and dried. Yield: 80%. *Anal*. Calc. for $C_{16}H_{16}O_8V$: C, 49.63; H, 4.16. Found: C, 49.9; H, 4.1%.

$[VO(Etsal)_2(H_2O)]$ (**2**): The compound was prepared as described above by using $VOSO_4$ and NaOH to increase the pH. Yield: ∼90%. *Anal*. Calc. for $C_{18}H_{20}O_8V$: C, 52.06; H, 4.85. Found: C, 52.2; H, 5.0%.

$[VO(sal)_2(H_2O)]$ (**3**): The compound was prepared as described for **2**. Yield: ∼90%. *Anal*. Calc. for $C_{14}H_{12}O_6V$: C, 51.39; H, 3.70. Found: C, 51.1; H, 3.5%.

2.3. X-ray crystallography for *1*

2.3.1. Crystal data
$C_{16}H_{14}O_7V.H_2O$, $M_r = 387.23$, monoclinic, space group $P2_1/n$, $a = 9.407(4)$, $b = 16.133(1)$, $c = 11.700(4)$ Å, $\beta = 111.46(1)°$, $V = 1652.5(9)$ Å^3, $Z = 4$, $F_{000} = 796$, $D_c = 1.556$ Mg/m^3, μ(Mo Kα) = 0.642 mm^{-1}.

2.3.2. Data collection
X-ray measurements were made with an Enraf-Nonius CAD-4 diffractometer and graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). Cell dimensions were determined from the measured θ values of 25 intense reflections with $12 < \theta < 15°$. The intensities of 3808 observations of 3595 independent reflections ($R_{int} = 0.0178$, $R_{sigma(I)} = 0.0410$) in the range $2.0 \le \theta \le 27.0°$ were measured by the $\omega/2\theta$-scan mode. The data was corrected for Lorentz, polarization and absorption effects.

The vanadium atom's position was determined by the Patterson method and the atomic positions of the remaining non-hydrogen atoms were calculated from a subsequent partial structure expansion, using the SHELXS-86 program [21]. Following convergence of the anisotropic refinement, all hydrogen atoms could be located from an electron density difference map, and were then included in the refinement with isotropic thermal motion parameters. The final refinement statistics are presented in Table 1.

The structure refinement calculations were carried out using the SHELXL-93 program [22]. Atomic scattering factors were taken from International Tables [23]. Selected bond lengths and angles are given in Table 2. Additional crystallographic data are available as Supplementary material.

3. Results and discussion

A molecular diagram presenting the atomic numbering scheme is shown in Fig. 1. Each molecule consists of two *o*-vanillin ligands that coordinate *cis* to the VO^{2+} group. The vanadium atom is six coordinate: the four equatorial coordination positions are filled by two phenolato O-atoms and two aldehyde carbonyl O-atoms, the axial ligand *trans* to the vanadyl O-atom being a water molecule. The geometry of the equatorial coordinating donor atoms is slightly pyramidal,

Table 1
Final refinement statistics for $[VO(o\text{-van})_2(H_2O)]$ (**1**)

Refinement method	full-matrix least-squares on F^2
Calculated weights	$w = 1/(\sigma^2(F_o^2) + (0.0410P)^2 + 0.59P)$
	$[P = (\max(F_o^2, 0) + 2F_c^2)/3]$
No. of refined parameters	290
No. unique reflections	3595
No. used reflections $[F > 0]$	3250
No. observed reflections $[F^2 > 2\sigma(F^2)]$	2537
R [F, observed data]	0.0431
R [F, used data]	0.0638
R [F, all data]	0.0795
wR [F^2, observed data]	0.0829
wR [F^2, used data]	0.0932
wR [F^2, all data]	0.1053
Goodness of fit, S [used data]	1.067
Goodness of fit, S [all data]	1.142
$\Delta\rho_{max}$ (e Å^{-3})	0.26(5)
$\Delta\rho_{min}$ (e Å^{-3})	−0.33(5)

Table 2
Selected bond distances (Å) and angles (°) in $[VO(o\text{-van})_2(H_2O)]$ (**1**)

V(1)–O(1)	1.596(2)	V(1)–O(2)	2.264(2)
V(1)–O(11)	1.964(2)	V(1)–O(17)	2.043(2)
V(1)–O(21)	1.950(2)	V(1)–O(27)	2.036(2)
O(1)–V(1)–O(11)	100.99(10)	O(1)–V(1)–O(21)	102.45(10)
O(1)–V(1)–O(17)	94.22(10)	O(1)–V(1)–O(27)	93.92(11)
O(11)–V(1)–O(17)	88.53(8)	O(21)–V(1)–O(27)	88.84(8)
O(11)–V(1)–O(21)	88.85(8)	O(17)–V(1)–O(27)	89.46(8)
O(11)–V(1)–O(27)	165.07(9)	O(17)–V(1)–O(21)	163.32(8)
O(1)–V(1)–O(2)	170.36(10)		

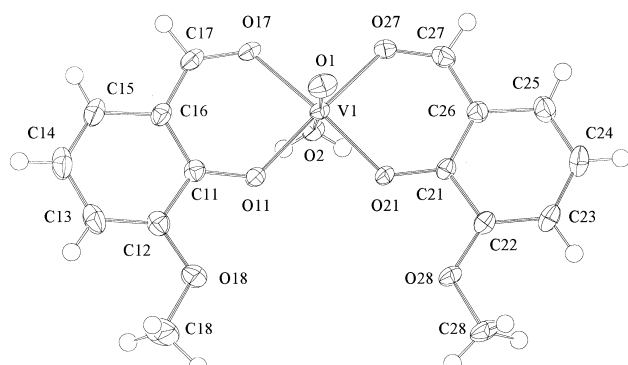Fig. 1. ORTEP [24] diagram of $[VO(o\text{-van})_2(H_2O)]$ (**1**) showing the atomic notation. The thermal ellipsoids of the non-hydrogen atoms have been drawn at the 30% probability level. The hydrogen atoms have been drawn with an arbitrary isotropic thermal parameter of $2.0\ \text{Å}^2$.

with the vanadium atom 0.275(8) Å from the least-squares plane defined by the four equatorial oxygen atoms.

Addison et al. [25] introduced the angular structural parameter, $\tau = (\beta - \alpha)/60$. In the present case, β corresponds to O(11)–V–O(27), α to O(17)–V–O(21) and $\tau = 0.017$, i.e. there is no significant trigonal-bipyramidal distortion of the square-pyramidal geometry corresponding to the vanadyl and the four equatorial bonds. The two o-vanillin ligands are nearly coplanar, the angle between the least-squares planes of the carbon atoms in each aromatic ring being 7.16(8)°. In addition, the o-vanillin ligands are only slightly tilted with respect to each other along the C(16)–C(26) direction, the dihedral angle defined by C(16), C(12), C(22) and C(26) being 3.8(1)°. As a result, the four oxygen atoms that coordinate the vanadium are close to being coplanar, with a dihedral angle between atoms O(17), O(11), O(21) and O(27) of 1.71(9)°. The molecules 'dimerize' about crystallographic inversion centres through the formation of bifurcated hydrogen bonds from the water hydrogens H(21w) and H(22w) to O(11) and O(18), and O(21) and O(28), respectively. The dimers pack in a staggered arrangement along the crystallographic c-axis. Geometrical details of the hydrogen bonds are given as Supplementary material.

3.1. UV–Vis spectra

The electronic spectrum of an approximately 1 mM solution of **1** in MeOH shows band I $(b_2(d_{xy}) \rightarrow e_\pi{}^*(d_{xz}, d_{yz}))$ at 830 nm $(\varepsilon = 30\ \text{dm}^3\ \text{cm}^{-1}\ \text{mol}^{-1})$ and band II $(b_2(d_{xy}) \rightarrow b_1{}^*(d_{x^2-y^2}))$ at around 580 nm $(\approx 17\,250\ \text{cm}^{-1})$ partly obscured by the tail of bands in the UV. Band III $(d_{xy} \rightarrow d_{z^2})$ occurs below 500 nm but is under a much stronger LMCT (possibly phenolate-O to d orbitals on the vanadium). The value of $10Dq$ can be estimated from the energy of the $b_2 \rightarrow b_1{}^*$ transition as $\nu_2 = 10Dq\ \sin^4\theta$, θ being the V=O equatorial ligand bond angle (e.g. [26]). It is similar to the one for $VO(acac)_2$ $(\approx 17\,000\ \text{cm}^{-1})$ (e.g. [27]) and slightly weaker than band II in $VO(\text{salicilato})_2$ $(\approx 17\,750\ \text{cm}^{-1})$. For **2** in MeOH, the visible spectrum is similar.

In the electronic spectrum of **3** (≈ 1 mM) in MeOH, bands I and II appear as shoulders of the much stronger LMCT band with $\lambda_{\max} \approx 780$ and 585 nm, respectively. Adding salicylaldehyde to this solution until an L:M ratio of 10, band I is clearly distinguished at ≈ 785 nm $(\varepsilon = 24\ \text{dm}^3\ \text{cm}^{-1}\ \text{mol}^{-1})$, but not band II. On adding base to this solution until pH 10, three bands appear in the visible range: 515sh, 610sh and 860 nm $(\varepsilon = 50, 18$ and $16\ \text{dm}^3\ \text{cm}^{-1}\ \text{mol}^{-1}$, respectively), probably corresponding to the formation of $[VO(sal)_2(OH)]^-$ with OH^- equatorial.

3.2. IR spectra

The V=O stretching frequencies are between 958 and 968 cm^{-1} in the typical range for oxovanadium(IV) compounds with the terminal, not bridging, oxo ligand. The $\nu(C=O)$ are around 1610–1630 cm^{-1} corresponding to a decrease of about 40 cm^{-1} compared with the free ligands. Bands around 1600–1610 and 1530–1550 cm^{-1} may be ascribed to ring vibrations, and bands at 735–760 cm^{-1} to C–H out-of-plane aryl-H bending vibrations; the values for **1**, **2** and **3** are consistent with the substitution patterns expected for four or three adjacent H atoms [28].

While **1** and **2** show only two medium intensity sharp bands at 3456, 3423 cm^{-1}, **3** presents a slightly broader band, centred at 3440 cm^{-1}, possibly due to $\nu(OH)$. In **3**, very weak sharp bands at 3020 and 2894 cm^{-1} may be due to the CH stretch of ethanol; the latter could also be ascribed to the C–H of the aldehyde group. In the FT-IR of **1** and **2**, apart from the weak sharp bands at $\approx 2885\ \text{cm}^{-1}$, which can be ascribed to aliphatic C–H stretch of the aldehyde group, a few weak bands in the range 2875–3000 cm^{-1}, stronger in **2**, are due to methyl C–H stretch of the OCH_3 and OC_2H_3 groups.

3.3. EPR spectra

The EPR spectra of **1** and **2** in methanol or of $EtOH/H_2O$ solutions containing VO^{2+}, ligand and acetate (1:2:2) are almost identical and denote rhombic or lower EPR symmetry. The spin-Hamiltonian parameters are presented in Table 3. The EPR spectra for **3**, under similar conditions, show no significant rhombicity and were simulated as axial. At pH ≈ 5.5, the spin-Hamiltonian parameters for the two species detected are compatible with **EI** corresponding to $[VO(sal)_2]$ and **EII** to $[VO(sal)(H_2O)]^+$. At pH ≈ 7 **EII** appears as a shoulder which corresponds to about 10–15% of **EI**.

Cornman et al. [29] discussed the differences of the spin-Hamiltonian parameters g_x, g_y and A_x, A_y as depending on trigonal-bipyramidal distortions of the complexes, and discussed this in terms of the angular structural parameter τ (see above). Complex **1** in the solid state is a typical case of an octahedral oxovanadium(IV) complex with a long bond *trans* to the oxo group, and the τ parameter is basically not applicable. Nevertheless in the context of the discussion that follows this parameter may be used. For **1**, in the solid state,

Table 3
Hyperfine coupling constants (cm^{-1}) and g values for the EPR spectra of frozen 'solutions' of complexes at 77 K

|		$A_z \times 10^4$	g_z	$A_x \times 10^4$	$A_y \times 10^4$	g_x	g_y
1 [a]		170.3	1.944	57	64	1.983	1.979
2 [a]		170.5	1.944	57.5	65.8	1.983	1.982
3 [b]	**EI**	169–170	1.935–1.947	≈ 65		≈ 1.982	
	EII	174–177	1.947–1.950	≈ 64		≈ 1.975	
3 [c]		≈ 171	≈ 1.950	≈ 63		≈ 1.981	

[a] By simulation with program EPRPOW, developed by Drs L.K. White and R.L. Belford (Univ. of Illinois) and modified by L.K. White, N.F. Albanese and N.D. Chasteen (Univ. of New Hampshire) to include both Lorentzian and Gaussian lineshape functions, an $I = 7/2$ nucleus, a 4th hyperfine interaction and multiple sites having different linewidths.

[b] Solid in methanol or in ethanol/water (pH ≈ 5.5): two species present: **EI** and **EII**, $\approx 50\%$ each.

[c] After addition of Hsal until a ligand-to-metal ratio of 10 at pH ≈ 7. A second minor species is present with higher hyperfine coupling constant (see text).

τ is small, i.e., there is no distortion of the bonding of equatorial ligands. If it is assumed that in solution the equatorial donor atoms are the same, as no significant intramolecular interactions are predicted, no distortions of the octahedral geometry are expected. However, the ligand field is not symmetric and mixing from the $3d_{z^2}$ orbital into the ground state is expected to contribute to the $g_\perp$ anisotropy (e.g. [30,31]).

Alternatively, the low EPR symmetry could be explained if **1** and **2** in MeOH or H$_2$O/EtOH solutions have coordination geometries such as schematically shown in **S-I** and not as in **S-II**. In this case, a separation of the d_{xz} and d_{yz} levels resulting in in-plane g anisotropy can occur (e.g. [32]).

S-I   **S-II**
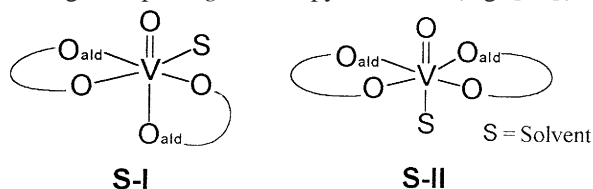
It is known that the parallel component of the hyperfine coupling constant is sensitive to the donor type in the 'equatorial' coordination sphere and an empirical additivity relationship (Eq. (1)) has been developed and frequently used as a means of determining, to a first approximation, the identity of the equatorial ligands in $V^{IV}O$ complexes [5,8,11,29,33]. In Eq. (1) n_i is the number of equatorial ligands of type i, and $A_{z,i}$ is the contribution from each equatorial ligand of type i. The empirical parameters $A_{z,i}$ have been determined for molecules of assumed square-pyramidal geometry but seem to be relatively insensitive to structural changes such as trigonal-bipyramidal distortions [29]. Additivity relationships have also been used to back-calculate the individual $A_{z,i}$ contributions for several donor groups such as N_{amide} and O_{amide} of simple dipeptides or model molecules [6,7,9,10], and N_{imine} in several Schiff base molecules [6,33].

$$A_z^{est} = \sum_{i=1}^{4} n_i A_{z,i} \qquad (1)$$

For the [VOL$_2$] complexes studied here, the $g_\parallel$ values are in the range 1.935–1.945 and $A_\parallel$ in the range 169–170.5 $\times 10^{-4}$ cm^{-1}. These are close to the values obtained

[34] for [VO(salicylato)$_2^{2-}$]: $g_\parallel = 1.948$ and $A_\parallel = 166.8 \times 10^{-4}$ cm^{-1}, the $A_\parallel$(Ar–C=O$_{aldehyde}$) being higher than $A_\parallel$(Ar–COO$^-$) and the $g_\parallel$ lower, in agreement with the known anti-correlation [5] between $A_\parallel$ and $g_\parallel$. This was also found for non-aromatic $A_\parallel$(O$_{carboxylate}$) and $A_\parallel$(O$_{amide}$) complexes, where $A_\parallel$(O$_{carboxylate}$) = 42.72×10^{-4} cm^{-1} [5] and $A_\parallel$(O$_{amide}$) = 43.67×10^{-4} cm^{-1} [8].

The difference in the $A_\parallel$ values of [VO(o-van)$_2$] (170.3×10^{-4} cm^{-1}) and [VO(salicylato)$_2$] (166.8×10^{-4} cm^{-1} [27]) is 3.5×10^{-4} cm^{-1}. If it is assumed (i) that both complexes in solution have all donor atoms equatorially coordinated, and (ii) that the difference in $A_\parallel$ is due solely to the presence of two O$_{aldehyde}$ instead of two O$_{carboxylate}$ donors (i.e. any variations in the orientation of the donor groups relative to the V=O axis would not change the $A_{z,i}$ values), then one could estimate the contribution of $A_\parallel$(Ar–O$_{aldehyde}$) in Eq. (1) as 44.47×10^{-4} cm^{-1}. This is consistent with the difference in bond lengths (≈ 0.03 Å) between V–O$_{aldehyde}$ and V–O$_{carboxylate}$ (normally 2.00–2.01 Å) and with the small difference in the energies of band II. This may also be compared with the contribution of $A_\parallel$(C=O) in 1,3-butanedionato complexes (42.7×10^{-4} cm^{-1} [35]), where increased in-plane π bonding is expected to correspond to a decreased $A_\parallel$ value.

4. Supplementary material

Additional crystallographic data and geometrical details are available from the authors on request.

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