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Synthesis, molecular structure and properties of oxo-vanadium(IV) complexes containing the oxydiacetate ligand

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The complex $[V(O)(oda)(H_2O)_2]$ **1** [oda = $O(CH_2COO^-)_2$] has been obtained by reaction of aqueous solutions of $[V(O)(acac)_2]$ with oxydiacetic acid. The coordination geometry around the vanadium in **1** is distorted octahedral with mutually *trans* water ligands and a planar conformation of the oda ligand (*mer*). The relative stability of the experimentally determined structure and that of the alternative isomer with a puckered oda conformation (*fac*) has been investigated by DFT calculations. The latter confirms that the *mer* geometry is more stable by 35.6 kJ mol^{-1}. The complex $[V(O)(oda)(\mu\text{-OMe})]_2[Na(H_2O)]_2$ **2a** is obtained by reaction of **1** with NaOH in methanol. The anions feature two V(O)(oda) units symmetrically bridged by methoxy groups in a *syn*-orthogonal arrangement, while the oda ligands have the *fac* conformation. Similar complexes $[V(O)(oda)(\mu\text{-OMe})]_2[K(H_2O)]_2$ **2b** and $[V(O)(oda)(\mu\text{-OMe})]_2[HL]_2$ **2c**–**2g** are obtained from reaction with KOH or with selected N-donor bases (L), respectively. An excess of pyridine, however, causes the simple substitution of the water molecules in **1** and generates the monomer $[V(O)(oda)(py)_2]$ **3**. Antiferromagnetic behaviour of binuclear compounds **2a**, **2d** and **2e** is suggested by a variable-temperature study. Finally, the reaction of **1** with bidentate N-donor ligands allows the synthesis of the complexes $[V(O)(oda)(N–N)]\cdot H_2O$ (N–N = 2,2′-bipyridine, **4**; *o*-phenanthroline, **5**). X-Ray characterization of **4** shows that the conformation of oda has changed from *mer* (as in the reactant **1**) to *fac*.

Introduction

The interest in the chemistry of oxovanadium complexes has grown enormously over the last few decades due to the role of vanadium in several biological processes.[1] In particular, the insulin-mimetic properties of some vanadium substrates have been extensively studied.[1,2] As a result of this research, a vanadium(IV) compound is being clinically tested as a potential treatment for a specific type of diabetes.[3] The precise knowledge of the chemical properties of new vanadium derivatives may provide valuable information with respect to the behaviour of such complexes in biological systems. Thus, the coordination chemistry of vanadium, in the high oxidation states (IV and V), continues to be intensively explored, as shown also by some recent contributions.[4]

In the course of our ongoing studies on transition metal complexes containing the oxydiacetate[5] and thiodiacetate ligands,[6] we decided to explore the oxydiacetate-vanadium system. We have already presented a preliminary report on the synthesis and biological properties of the complex $[V(O)(oda)(H_2O)_2]$ **1** [oda = $O(CH_2COO^-)_2$].[7] Subsequently, the reactivity of this compound has been tested and a number of different products have been obtained. This paper reports all of our findings in detail. Thus, we start from a complete report of the synthesis, structure and properties of the parent compound **1**. The structural flexibility of the latter has also been analysed by DFT calculations that allow an evaluation of the different energetics between the alternative conformers [planar (*mer*) or puckered (*fac*) arrangement of the ligand oda]. Further, the reactivity of **1** toward different bases has been tested in methanol solutions. Generally, dimeric species with bridging methoxy groups are obtained (*e.g.*, $[V(O)(oda)(\mu\text{-OMe})]_2[Na(H_2O)]_2$ **2a**) for some of which (**2a**, **2d** and **2e**) a study of the temperature dependent magnetism has been undertaken. Monomeric products are obtained only if pyridine (excess) or bidentate N–N donor ligands (2,2′-bipyridine or *o*-phenanthroline) are used as bases. Compounds such as $[V(O)(oda)(py)_2]$ **3** and $[V(O)(oda)(N–N)]\cdot H_2O$ (N–N = bipy, **4**; phen, **5**) will also be described.

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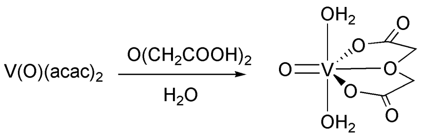
Results and discussion

Synthesis, characterization and molecular structure of 1

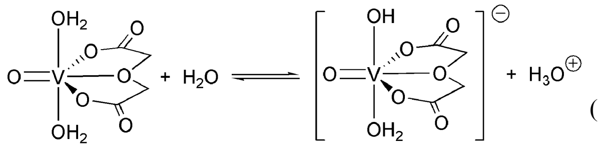
Some studies on the stability of the vanadyl–oxydiacetic acid aqueous system were reported as early as 1973[8] and 1980.[9] These studies were restricted to the behaviour in solution and no information about the composition and structure of the vanadium(IV) species was provided. In order to identify the nature of these systems, we have synthesized and isolated a vanadium(IV) complex containing the oxydiacetate ligand. Treatment of aerobic aqueous solutions of $[V(O)(acac)_2]$ with oxydiacetic acid, $O(CH_2COOH)_2$, yields, after the appropriate work up, blue crystals of $[V(O)(oda)(H_2O)_2]$ **1** in good yields [eqn. (1)].



1

(1)

The IR spectrum of **1** displays the characteristic absorptions of the vanadyl group and water ligands. In addition, a very strong and broad band at about 1590 cm^{-1} corresponds to the antisymmetric vibration of the COO^- groups while the symmetric vibrations correspond to the strong band appearing at 1424 cm^{-1}. It has been recently proposed,[5] that the IR band corresponding to the antisymmetric COC stretching at the ethereal oxygen can be discriminative of the coordination mode adopted by the oxydiacetate ligand. For **1**, this band appears at 1136 cm^{-1}, *i.e.* in the region appropriate for the planar disposition of oda (*mer*). The measured effective magnetic moment, both in solution and in the solid state, is *ca.* 1.7 μ_B, consistent with a d^1 ground-state electronic configuration for the metal. Complex **1** is stable to air in the solid state and, also, in H_2O solutions. The latter remain unaltered (UV-VIS control) after bubbling of oxygen for one day. Also, hydrogen–deuterium exchange occurs (IR control) as confirmed by formation of the deuterated complex $[V(O)(oda)(D_2O)_2]$ upon dissolution of **1** in D_2O and subsequent crystallization (see Experimental). The aqueous solution of **1** is characterized by an acidic pH which is probably due to a hydrolysis process [eqn. (2)]. Similar behaviour has also been observed for related systems, such as those of oxovanadium(IV)–iminodiacetate.[10]



1

(2)

The molecular structure of **1** has been determined by X-ray diffraction methods. Fig. 1 presents a portion of the intermolecular network highlighting the intermolecular hydrogen bonds between one uncoordinated oxygen atom of carboxylate and one coordinated water molecule. The first column of Table 1 reports selected bond lengths and angles of the present structure. Each complex molecule possesses an inner twofold axis coinciding with the vanadyl group and the central oxygen atom of oda. The coordination geometry of vanadium is pseudo-octahedral. The water ligands are mutually *trans* [O4–V–O4′ = 174.3(2)°] while the oxydiacetate ligand is meridionally distributed. A similar *mer* disposition of oda has been found in many octahedral transition metal complexes.[11,12] Ideal octahedral geometry cannot be achieved as the adjacent bites of the tridentate oda ligand (O3–V–O2 angles) are only 73.05(8)°. The vanadyl bond length is 1.586(5) Å and compares well with the average value of 1.600(1) Å resulting from the over 1000 corresponding structures deposited with the CCDC.[13] The other vanadium–oxygen bond distances are 2.042(2) Å (water ligands), 2.017(2) Å (carboxy groups) and 2.176(5) Å (ethereal oxygen atom O2). The stereochemistry of **1** resembles that of the analogous complex $[V(O)(dipic)(H_2O)_2]$ (dipic = pyridine-2,6-dicarboxylate).[14]

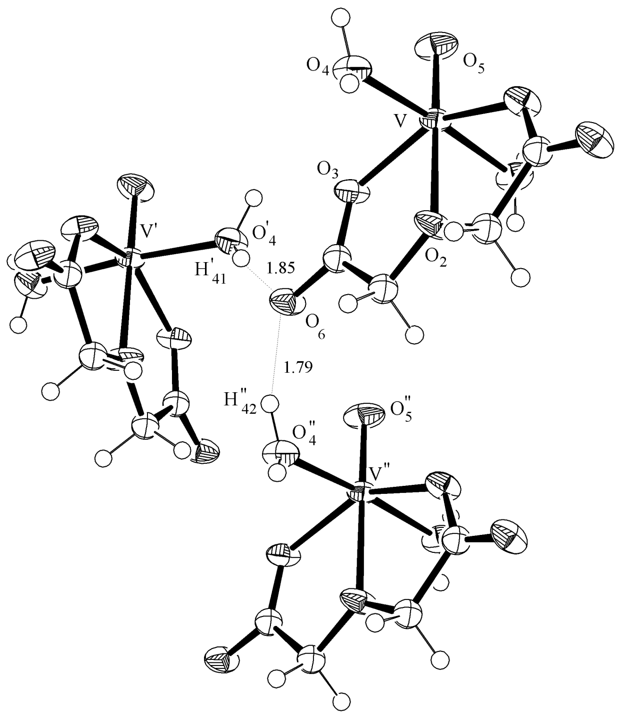


Fig. 1 ORTEP drawing showing three symmetry related molecules of $[V(O)(oda)(H_2O)_2]$ **1** that are interconnected by hydrogen bonds. Each molecule possesses a twofold axis whereas different molecules are related by glide planes.

Table 1 Selected bond distances (Å) and angles (°) for $[V(O)(oda)(H_2O)_2]$[a]

Structural data	Experimental Complex **1**	Calculated *mer* isomer	Calculated *fac* isomer
V–O5	1.586(5)	1.589	1.580
V–O2	2.176(5)	2.247	2.435
V–O3	2.017(2)	1.925	1.922
V–O3′		1.932	1.917
V–O4	2.042(2)	2.132	2.150
V–O4′		2.124	2.157
O3–C1	1.268(4)	1.321	1.315
O3′–C1′		1.322	1.320
O6–C1	1.246(4)	1.219	1.220
O6′–C1′		1.218	
C1–C2	1.505(4)	1.542	1.538
C1′–C2′			1.545
O2–C2	1.414(4)	1.425	1.440
O2′–C2′		1.424	1.447
O5–V–O2	180.000(1)	178.4	177.2
O5–V–O3	106.95(9)	106.1	108.3
O5–V–O3′		106.2	103.3
O5–V–O4	92.84(9)	95.7	100.1
O5–V–O4′		94.8	96.1
O3–V–O4		85.8	81.8
O3′–V–O4′		93.1	84.3
O3–V–O4′	88.46(9)	88.1	148.5
O3′–V–O4		87.2	157.9
O2–V–O3	73.05(8)	74.1	75.7
O2–V–O3′		73.7	74.3
O2–V–O4	87.16(9)	85.9	78.4
O2–V–O4′		83.7	86.0
O3–V–O3′	146.09(17)	147.5	101.6
O4–V–O4′	174.32(17)	169.4	82.0
C2–O2–C2′	121.6(4)	120.3	113.4
O6–C1–O3			
O6′–C1′–O3′	123.8(3)	125.5	125.7
O6–C1–C2	117.8(3)	119.9	119.3
O6′–C1′–C2′		120.1	119.7
O3–C1–C2	118.4(2)	114.5	115.0
O3′–C1′–C2′		114.4	114.6
O2–C2–C1	105.5(3)	107.2	111.2
O2′–C2′–C1′		106.9	111.3

[a] Primed atoms are related to unprimed equivalents by the symmetry transformation $-x + 2, -y, z$.

DFT calculations for models of compound 1

In order to gain a deeper insight into the structural features of **1**, DFT calculations were carried out. Two different arrangements of the oxydiacetate ligand were considered that correspond to the experimental *mer* conformation of oda and to one possible *fac* isomer with the vanadyl group also *trans* to the oda's ethereal oxygen atom. The optimised geometries of these isomers are depicted in Fig. 2, while, in Table 1, the structural

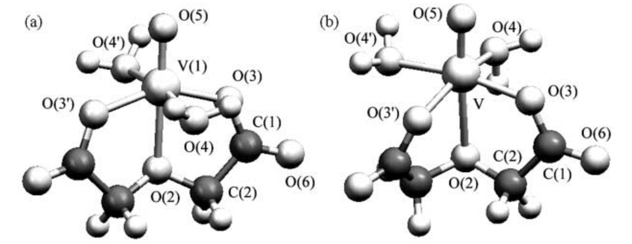


Fig. 2 Computed isomers of **1** with (a) *mer* and (b) *fac* conformations of ligand oda, respectively.

parameters are compared with those of the experiment. As seen, the agreement with the computed *mer* structure is reasonably good. Bond angles are within 5°, while only the V–O_{water} distances are overestimated by about 0.08 Å. The other lengths, including C–C and C–O bonds, are acceptable with a somewhat pronounced asymmetry of the two carboxylate C–O distances in the computed structure. The same observations apply also to the *fac* isomer, where the V–O_{water} distance is again rather long and even more asymmetric C–O bonds are observed for the COO groupings (1.22 and 1.32 Å, respectively). A remarkable difference between the two calculated conformers is the elongation [from 2.247 (*mer*) to 2.435 Å (*fac*)] of the V–O2 bond *trans* to V=O group. Although the *fac* isomer of **1** is not isolated experimentally, the trend is confirmed by the definitely longer V–O_{ether} bonds in the complexes **2a** or **4** found to adopt the *fac* conformation (*vide infra*).

The flexibility of the oda ligand in coordinating a transition metal centre was computationally tested by us for the nickel complex [Ni(oda)(H_2O)$_3$].[5] A rather small energy difference ($\Delta E = 8.4$ kJ mol^{-1}) between *fac* and *mer* isomers was computed although only the former conformation is experimentally observed. In this case, the computed ΔE value is larger (about 35.6 kJ mol^{-1}) and likely sufficient to account for the experimental observation of the *mer* conformer. Also, the preferred planar conformation of ligand oda can be explained by the same qualitative argument used for the nickel compound.[5] Essentially, the electron pair donated from the ethereal oxygen atom is better oriented to attain a greater overlap with the empty metal σ orbital hybrid when the conformation is *mer*. In the present case, the difference between the two M–O_{ether} bonds (always *trans* to the V=O group) is as large as *ca.* 0.19 Å whereas it was only 0.11 Å in the nickel case. This may very well account for the significantly different ΔE values in the two cases.

Finally, the calculated IR spectra of the *mer* and *fac* conformers were analyzed with special consideration for the absorptions corresponding to the COC antisymmetric stretching frequencies. The computed IR band appears at 1151 and 1058 cm^{-1} for the *mer* and *fac* isomers, respectively. The former fits well with the experimental value of 1136 cm^{-1} found for **1**. This result supports satisfactorily our previous suggestion that oda conformations in a transition metal complex can be discriminated on the basis of IR spectra.[5]

Reactivity of 1 *versus* selected bases: synthesis of dinuclear derivatives 2a–2g, molecular structure of 2a and magnetic properties

As stated before, aqueous solutions of complex **1** are acidic. A chemical transformation is observed after treatment of these solutions with sodium hydroxide. The reaction is reversible and complex **1** forms again (IR control) upon the addition of the equivalent amount of acid (HCl). All the attempts to isolate a single stable product in the reaction with NaOH were unsuccessful when water was used as solvent. However, the result is different when methanol is employed. In this case, treatment of [V(O)(oda)(H_2O)$_2$] **1** with sodium hydroxide gives, after work up, dark blue crystals of the compound [V(O)(oda)(μ-OMe)]$_2$[Na(H_2O)]$_2$ **2a**. A similar species, [V(O)(oda)(μ-OMe)]$_2$[K(H_2O)]$_2$ **2b**, was obtained using KOH as reagent. The IR spectrum of **2a** displays two strong and broad absorptions at 1663 and 1395 cm^{-1} that may be assigned to antisymmetric and symmetric vibrations of the carboxylate groups, respectively. Additionally, a sharp absorption appears at 1112 cm^{-1}, which can be attributed to the antisymmetric COC stretching of the oda ligand. This value is lower by *ca.* 24 cm^{-1} than that of complex **1** and suggests a change in the bonding mode of the oda ligand from *mer* to *fac* conformation.[5] Equivalent IR absorptions bands were observed for the analogous derivative **2b**.

The X-ray structure of compound **2a** has been determined and selected bond distances and angles are reported in Table 2.

Table 2 Selected bond distances (Å) and angles (°) for the anion of complex **2a**

V1–O1	1.600(9)	O2–C1	1.291(12)
V1–O9	1.961(8)	O3–C2	1.422(12)
V1–O2	2.012(7)	O4–C4	1.394(15)
V1–O3	2.247(9)	O5–C3	1.283(13)
V1 ··· V2	3.100(3)	O10–C1	1.242(13)
V2–O6	1.584(9)	O9–C5	1.469(16)
V2–O9	1.968(7)	C1–C2	1.490(15)
V2–O5	2.011(7)	C3–C4	1.489(18)
V2–O4	2.340(10)		
O1–V1–O9	105.8(4)	O9–V2–V1	37.8(2)
O1–V1–O2	94.7(3)	O5–V2–V1	127.5(2)
O9–V1–O2	157.5(3)	O4–V2–V1	86.9(3)
O1–V1–O3	163.5(4)	C1–O2–V1	121.9(7)
O9–V1–O3	87.1(3)	C2–O3–V1	112.1(6)
O2–V1–O3	74.7(3)	C4–O4–V2	109.5(7)
O1–V1–V2	107.9(4)	C3–O5–V2	124.6(6)
O9–V1–V2	38.0(2)	C5–O9–V1	126.9(8)
O2–V1–V2	126.7(2)	C5–O9–V2	126.5(8)
O3–V1–V2	88.6(3)	V1–O9–V2	104.2(3)
O6–V2–O9	105.1(5)	O10–C1–O2	123.7(10)
O6–V2–O5	97.5(4)	O10–C1–C2	119.5(10)
O9–V2–O5	91.5(3)	O2–C1–C2	116.8(9)
O6–V2–O4	166.2(6)	O3–C2–C1	111.1(9)
O9–V2–O4	85.7(3)	O5–C3–C4	115.3(10)
O5–V2–O4	73.3(3)	O4–C4–C3	114.2(12)
O6–V2–V1	106.9(5)		

Fig. 3 presents a portion of the crystalline arrangement that consists of [V(O)(oda)(μ-OMe)]$_2^{2-}$ anions and interspersed sodium cations. In the dinuclear anion, having an inner mirror plane, the vanadium atoms are held together by two bridging methoxy groups. The two vanadyl groups eclipse each other and are therefore in the *syn*-orthogonal conformation defined by Plass.[15] The ligand oda completes six-coordination at each metal. As already suggested by the IR spectra, each oxydiacetate ligand adopts a *fac* disposition with its ethereal oxygen atom occupying the *trans* position with respect to the oxo ligand. Similar *fac* configuration of the oda ligand has been previously observed only in some nickel[11i] and copper complexes.[11a,b] The V(1)–V(2) distance is long, 3.100(3) Å, and excludes any major covalent bonding between the metals. The Na^+ cations are hepta-coordinated by the oxygen atoms of two water molecules, by three uncoordinated oxygen atoms of different carboxylate groups and by one carboxylate acting as a chelate. The separation between two cations, bridged by the oxygen atoms O7, O8 and O10, is 3.466(3) Å. A similar value

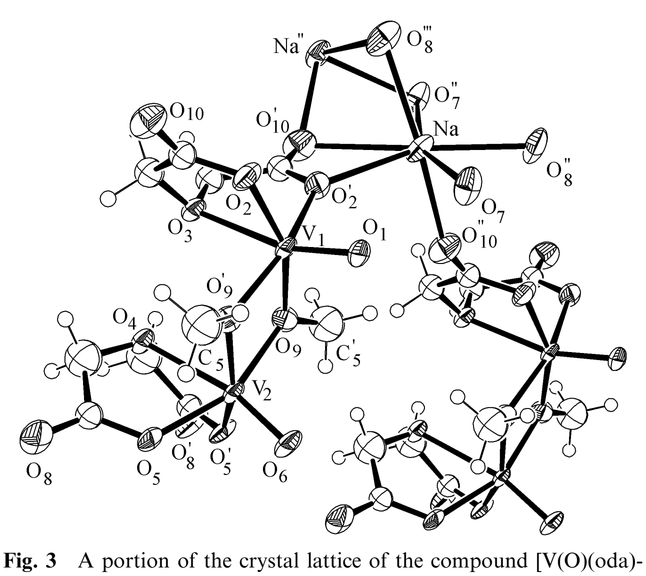
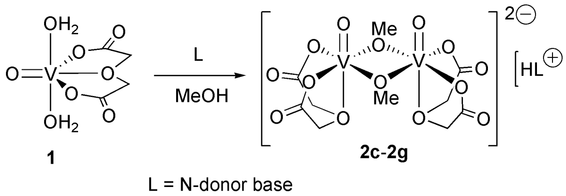


Fig. 3 A portion of the crystal lattice of the compound [V(O)(oda)(μ-OMe)]$_2$[Na(H_2O)]$_2$ **2a**. Two dinuclear dianions, having an inner symmetry plane, are shown together with interspersed sodium cations and water molecules (O7).

was found in [V(O)(3-hydroxy-3-methylglutarate)]$_2$Na$_2$.[16] While five Na–O distances are in the range 2.36–2.46 Å, those involved with the chelating carboxylate group are longer [2.611(9) and 2.719(9) Å for Na–O10 and Na–O2, respectively].

The reactivity of **1** towards other bases has also been tested. The interaction of **1** with monodentate N-donor reagents (L) in methanol gives complexes similar to **2a** and **2b** of general formulation [V(O)(oda)(μ-OMe)]$_2$[HL]$_2$ (L = 2-methylpyridine, 2-Mepy, **2c**; 2,6-dimethylpyridine, 2,6-Me$_2$py, **2d**; 4-dimethylaminopyridine, 4-Me$_2$Npy, **2e**; NEt$_3$ **2f**; and PhNH$_2$, **2g**) [eqn. (3)]. The observation of similar IR patterns for all these compounds suggest that they all have the same structure found for complex **2a**. Different reaction patterns are followed when a large excess of pyridine is added to a methanol solution of **1**. Complex [V(O)(oda)(py)$_2$] **3** was isolated as a blue solid almost insoluble in any solvent but pyridine and water. In the latter case, however, the pyridine ligands are displaced again by the water molecules and compound **1** is formed.



(3)

At room temperature, the value of the effective magnetic moments of the complexes **2a**–**g** are those expected for a d^1–d^1 system. This fact is in conformity with other similar dimers reported in the literature.[17] We have selected three compounds, **2a**, **2d** and **2e**, for studying the variation of their magnetic behaviour with the temperature. We have monitored the variation of the magnetic susceptibility for crystalline samples of **2a**, **2d** and **2e** in the temperature range 4–290 K. The $\chi_M T$ (for two vanadium atoms) *versus* T values are plotted in Fig. 4. For complex **2a**, the $\chi_M T$ value at room temperature diminishes slightly when the temperature decreases in the range 290–50 K. After the lower limit, the $\chi_M T$ values decrease quickly and reaches the value of 0.33 cm^3 mol^{-1} K at 4 K. For the complexes **2d** and **2e**, the $\chi_M T$ value at room temperature diminishes quickly when the temperature decreases and reaches approximately zero at 4 K. This behaviour is indicative of weak antiferromagnetic coupling in the case of **2a** and strong in the case of **2d** and **2e**. The susceptibility data were fitted by using an expression of the Bleaney–Bowers type for dinuclear $S = ½$ compounds,[18] based on the spin Hamiltonian $H = -2JS_AS_B$. The result of the fit, shown as the solid line in Fig. 4, was $2J = -12.0(1)$ cm^{-1}, $g = 1.89(1)$ for **2a**; $2J = -105.6(1)$ cm^{-1}, $g = 2.14(1)$ for **2d** and $2J = -76.0(1)$ cm^{-1}, $g = 1.97(1)$ for **2e**.

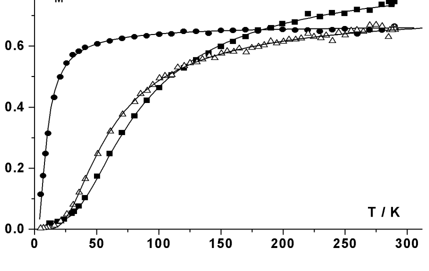
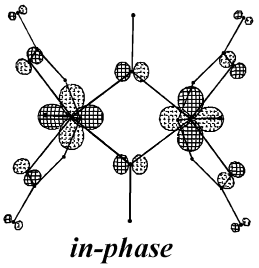


Fig. 4 Temperature dependence of the $\chi_M T$ values for **2a** (solid circles), **2d** (solid squares) and **2e** (open up triangles). Solid lines show the best fit indicated in the text.

It is of general interest for transition metal dimers[19] to establish any possible correlation between structural parameters and the magnetic exchange. In particular, for dinuclear vanadium d^1–d^1 derivatives containing oxygen atoms as bridges some attempts to correlate the magnetic data with structural parameters have been reported. For example, Carrano and co-workers[20] correlate the dihedral angle between the VO$_2$ and PO$_2$ planes of the V(OPO)$_2$V ring and the coupling constant in several tris(pyrazolylborate)–vanadium(IV) dimers that contain bridging substituted phosphate ligands. Also, Ceccato and co-workers[21] show, for dinuclear μ-OR bridging octahedral oxovanadium(IV) complexes, a relationship that involves the coupling constant and the dihedral angle between the equatorial planes.

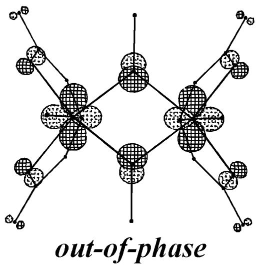
Table 3 summarizes selected structural details and the coupling constant $-2J$ for ten comparable oxovanadium(IV) dimers containing two bridging μ-OR groups, including complex **2a**. All of them have as a common feature an orthogonal configuration according to Plass.[15] As indicated in one of the columns, the V(μ-OR)$_2$V framework is not exclusive for six-coordinated metal centres as there are also examples of a local square pyramidal environment. We have tried to analyse the dependence of the magnetic data with (i) the intermetallic distance, (ii) the V–O–V angles at the bridges, and (iii) the distortion from planarity of the V(μ-OR)$_2$V framework (ring puckering).

As a general result for this series of compounds, there cannot be any appreciable correlation between the $-2J$ coupling constant and the puckering of the V(μ-OR)$_2$V ring. In fact, all of the frameworks are practically planar with the single exception of {[V(O)(μ-OH)]$_2$(tpen)}I$_2$·2H$_2$O.[17c] More indicative are the trends for the V–V distances and for the bridging angles V–O–V. In general, $-2J$ increases when the V–V distance or the V–O–V angles diminish. A simple overlap model can provide a qualitative explanation. In the pseudo-octahedral local geometry, the single electron of each vanadium(IV) metal occupies a d$_{xy}$ metal orbital. In fact, the remaining pseudo-t$_{2g}$ orbitals (xz and yz) are somewhat destabilized by π interactions with the oxo ligand. Drawings of the two magnetic orbitals (in-phase and out-of-phase) are shown in **I** and **II** (below) as generated by an EHMO calculation[26] for an idealized C_{2v} model of **2a**.



in-phase

I



out-of-phase

II

It is evident that both the MOs, separated in energy by only 18.3 kJ mol^{-1}, have a significant participation of the symmetry adapted combinations of the methoxy groups. If the V–O–V angle varies, the energy variation of these molecular orbitals will be essentially governed by the d$_{xy}$(vanadium)–2p(oxygen) overlap in the same way that in the classical planar hydroxo-bridged copper(II) dimers.[19b,27] In a very qualitative manner, it may be argued that both the through-bridge and through-space interactions govern the antiferromagnetic coupling, in agreement with the classic super-exchange mechanism.[19]

In spite of the above efforts to correlate the magnetic coupling constant with some selected geometric parameter, in no case was a satisfactory linear dependence observed. Thus it is likely that the system is sensitive to factors other than the geometric ones that have been considered by us. For instance, the simple change of the cation in the complexes **2d** and **2e**, with respect to **2a**, increases significantly the value of the $2J$ constant from -12.0 to -105.6 and -76.0 cm^{-1}, respectively.

Table 3 Selected magnetic properties and structural data of some dinuclear oxovanadium(IV) complexes with an orthogonal conformation

		Structural data					
Compound and refcode	$-2J$/cm^{-1}	Conformation: orthogonal	Local coordination number	d(V ··· V)/Å	V–O–V/°	V(μ-OR)$_2$V puckering/°	Ref.
$[V(O)(oda)(\mu\text{-}OMe)]_2[Na(H_2O)]_2$ **2a**	12.0	*syn-*	6	3.101(3)	104.2(3)	175	This work
$\{[V(O)]_2(\mu\text{-}OC_6H_3\text{-}2,6\text{-}dicarboxylate)[K(dmso)]_2\}_n$ TOLCEC	46.8	*anti-*	5	3.123(1)	104.8	180	22
$[V(O)(3\text{-hydroxy-3-methylglutarate})]_2Na_2\cdot 3H_2O\cdot MeOH$ YICZAT	60	*anti-*	5	3.107(3)	104.8(4) 104.7(4)	180	16
$\{[V(O)]_2(citrato)(Hcitrato)\}K_3\cdot 7H_2O$	74.8	*syn-*	5	3.026(2)	99.0(2) 101.1(2)	Not reported	23
$[V(O)(\mu\text{-}OH)(Tp)]_2$ RELMAW	77.6	*anti-*	6	3.122(5)	103.2(2)	180	20
$[V(O)(\mu\text{-}OMe)(maltolato)]_2$ PUTBAH	214	*anti-*	5	3.0806(6)	103.8	180	24
$\{[V(O)(\mu\text{-}OH)]_2(tpen)\}I_2\cdot 2H_2O$[a] VAFZAD	300	*syn-*	6	2.965(6)	97.8(6) 98.3(7)	160	17c
$[V(O)(BBAC)]_2[HNEt_3]_2\cdot 2CH_2Cl_2$[b] DOTQAE	335.8	*anti-*	6	3.125	98.62(7)	180	21
$[V(O)(\mu\text{-}OH)(1,4,7\text{-triazacyclononane})]_2Br_2$ CINKUF	354	*anti-*	6	3.033(3)	101.2(2)	180	17b
$\{[V(O)]_2(citrato)(Hcitrato)\}(Hneo)_3\cdot 4H_2O$[c] REPPOR	424	*syn-*	5 and 6	2.949(1)	94.8(2) 97.2(2)	171	25

[a] tpen = *N,N,N′,N′*-tetrakis(2-pyridilmethyl)ethylendiamine. [b] H3BBAC = *N,N*-bis(2-hydroxybencyl)aminoacetic acid. [c] neo = 2,9-dimethyl-1,10-phenanthroline.

Unfortunately, no crystals suitable for X-ray diffraction analysis have been obtained for **2d** and **2e** and we could not verify whether the presence of the cations $[H(2,6\text{-}Me_2py)]^+$ or $[H(4\text{-}Me_2Npy)]^+$ respectively affects significantly the geometry of the V(μ-OMe)$_2$V dimeric framework. Since in **2a**, the Na^+ ions are coordinated by some oda oxygen atoms also bound to vanadium metals, it is likely that at least the secondary structure of the dimer (bond distances and angles) may be affected with consequences for the magnetic behaviour.

Reactivity of compound 1 *versus* bidentate N-donor ligands

It has been found that the two coordinated water molecules of complex **1** are easily displaced by reaction with bidentate N-donor ligands. In fact, solutions of **1** react with 2,2′-bipyridine (bipy) and *o*-phenanthroline (phen) to give complexes of general formula [V(O)(oda)(N–N)] (N–N = bipy, **4**; phen, **5**). Both complexes can be isolated in good yields as crystalline solids and both are found to contain one water molecule of hydration. Complexes **4** and **5** may be dissolved in water but are not soluble in solvents of low polarity. They are air stable, both in solution and in the solid state. The effective magnetic moment values of these derivatives are similar to that of **1** and consistent with one unpaired electron in the ground-state configuration.

The X-ray structure of compound **4** has been determined. Fig. 5 shows the two independent molecules found in the asymmetric unit and highlights the hydrogen bonds between the water molecules of crystallization and uncoordinated carboxylate oxygen atoms. A summary of bond distances and angles is presented in Table 4. Essentially, there are no major structural differences between the two independent molecules of [V(O)(oda)(bipy)] **4**. The vanadium metal has a distorted octahedral environment. The ligand oda adopts the *fac* disposition and, similarly to **2a**, the central oxygen atom lies *trans* to the oxo group. The corresponding V–O$_{\text{ether}}$ bond distances

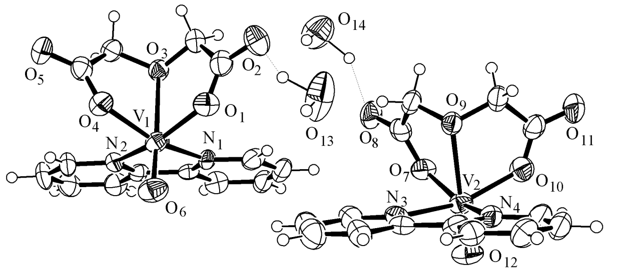


Fig. 5 The two independent molecules present in the lattice of [V(O)(oda)(bipy)]·H$_2$O **4**. The drawing highlights the hydrogen bonds between one water of crystallization and one uncoordinated carboxylate oxygen atom of oda.

Table 4 Selected bond distances (Å) and angles (°) for complex **4**

Molecule 1			
V1–O1	1.973(6)	O1–C1	1.266(10)
V1–O3	2.316(5)	O2–C1	1.224(10)
V1–O4	1.976(5)	O3–C2	1.424(9)
V1–O6	1.580(6)	O3–C3	1.439(9)
V1–N1	2.117(6)	O4–C4	1.283(10)
V1–N2	2.092(6)	O5–C4	1.209(9)
O1–V1–O6	101.6(3)	O1–V1–N1	89.4(2)
O4–V1–O6	101.1(3)	N1–V1–N2	77.5(2)
O1–V1–O4	93.7(2)	O6–V1–O3	174.3(2)
O6–V1–N2	100.3(3)	O1–V1–O3	75.3(2)
O1–V1–N2	156.5(2)	O3–V1–O4	74.5(2)
O4–V1–N2	90.3(2)	N1–V1–O3	82.1(2)
O6–V1–N1	102.8(3)	N2–V1–O3	83.6(2)
O4–V1–N1	154.7(2)		
Molecule 2			
V2–O7	1.975(5)	O7–C15	1.296(10)
V2–O9	2.334(5)	O8–C15	1.219(9)
V2–O10	1.987(6)	O9–C17	1.427(9)
V2–O12	1.571(6)	O9–C16	1.434(9)
V2–N3	2.096(7)	O10–C18	1.257(10)
V2–N4	2.104(7)	O11–C18	1.225(10)
O7–V2–O12	101.5(3)	O10–V2–N4	89.2(2)
O10–V2–O12	102.7(3)	N3–V2–N4	77.7(2)
O7–V2–O10	93.0(2)	O12–V2–O9	175.6(2)
O12–V2–N3	100.1(3)	O7–V2–O9	75.2(2)
O7–V2–N3	91.0(2)	O9–V2–O10	74.8(2)
O10–V2–N3	155.6(3)	N3–V2–O9	83.0(2)
O12–V2–N4	101.4(3)	N4–V2–O9	82.3(2)
O7–V2–N4	155.9(2)		

[2.316(5) and 2.334(5) Å] are appreciably longer than the analogous distance in complex **1** [2.176(5) Å], where the oda ligand is planar, but are in good agreement with the comparable bonds in complex **2a**. The separations corresponding to the hydrogen bonds O(14)–H ··· O(8) and O(13)–H ··· O(2) are 1.75(1) and 1.82(1) Å, respectively. The overall disposition of the ligands in **4** is similar to that found in complex [V(O)(ida)(bipy)] (ida = iminodiacetate).[28] Also, an interesting comparison can be made with the complex [V(O)(dipic)(phen)][29] where the ligand dipic (pyridine-2,6-dicarboxylate) can be considered the analogue of oda. In the latter, one phenanthroline N donor lies *trans* to the V=O group at variance with the situation in **4** where both the bipy nitrogen atoms are *cis* to the oxo ligand. This is not attributable to the different donor capabilities between bipy and phen but likely to the difficult adaptability of dipic to the *fac* disposition. Further support for this viewpoint comes from an X-ray study of complex **5**. In actuality, the quality of the crystals and of the structural refinement is too poor to be presented in detail. However, all of the heavier atoms were unambiguously located and it may be safely concluded that replacement of bipy for phen does not induce any major change of the primary structure with oda in the *fac* conformation.

Experimental

All preparations and other operations were carried out under aerobic conditions. Microanalyses (C, H, N) were carried out by the Microanalytical Service of the Instituto de Investigaciones Químicas (CSIC). Infrared spectra were recorded on a Perkin-Elmer Model 883 spectrophotometer (KBr pellet or Nujol emulsion in NaCl plates). Magnetic moments were measured, at room temperature, in the solid state with a Sherwood Scientific (Cambridge Research Laboratory) magnetic balance or in solution by the Evans method.[30] Magnetic susceptibility measurements in the temperature range 4–300 K were carried out on polycrystalline samples with a pendulum type magnetometer (MANICS DSM8) equipped with a helium continuous-flow cryostat and a Bruker B E15 electromagnet. The magnetic field was *ca.* 1.5 T. Diamagnetic corrections were estimated from Pascal′s constants. The EPR spectra were recorded at room temperature on a Bruker ES200 spectrometer at X-band frequency. Oxydiacetic acid and other chemicals were obtained from commercial sources and were used without further purification. The petroleum ether used had bp = 40–60 °C.

Syntheses

[V(O)(oda)(H_2O)$_2$] 1. Water (100 ml) was added to a solid mixture of VO(acac)$_2$ (10.6 g, 40 mmol) and O(CH_2COOH)$_2$ (5.36 g, 40 mmol). The resulting mixture was heated at reflux for 3 h. The hot solution was filtered, concentrated (in order to eliminate by evaporation the Hacac) and slowly cooled. Blue crystals of **1** were filtered off, washed with acetone and Et_2O and dried (7.5 g, 80%). IR (KBr/cm^{-1}): 3056–2887 very br ν(OH), 1590 s br ν(COO asymm), 1424 s ν(COO symm), 1136 s ν(COC asymm), 994 s ν(VO). μ_{eff} (solid state) = 1.71 μ_B. μ_{eff} (H_2O–^{t}BuOH solution, 9 : 1) = 1.68 μ_B. UV-VIS (H_2O): λ_{max}/nm: 275, 790. (Found: C, 20.60; H, 3.21. $C_4H_8O_8V$ requires C, 20.43; H, 3.40%). Deuterated complex [V(O)(oda)(D_2O)$_2$] was obtained by stirring a solution of **1** in D_2O for 15 min and subsequent crystallization of the solution at room temperature. IR (KBr/cm^{-1}): 2298 and 2188 br ν(OD).

[V(O)(oda)(μ-OMe)]$_2$[Na(H_2O)]$_2$ 2a. A solution of [VO(oda)(H_2O)$_2$] **1** (0.47 g, 2 mmol) in MeOH (15 ml) was added to a finely powdered solid NaOH (0.08 g, 2 mmol). A blue solid was formed and the resulting mixture stirred for 20 min. The precipitate was decanted, washed with MeOH, acetone and Et_2O and dried. The resulting solid was dissolved in a mixture of MeOH–H_2O (5 : 2 ml, respectively) and the resulting solution was kept at room temperature overnight. Deep blue crystals of **2a** were obtained (0.32 g, 60%). IR (KBr/cm^{-1}): 3552, 3417 br ν(OH), 1663 s br ν(COO asymm), 1395 s ν(COO symm), 1112 s ν(COC asymm), 993 s ν(VO). μ_{eff} (solid state) = 2.45 μ_B. EPR powder spectrum: broad isotropic signal centred at g = 1.99 (peak-to-peak line-width 357 G). (Found: C, 21.51; H, 3.18. $C_{10}H_{18}O_{16}Na_2V_2$ requires C, 21.24; H, 3.54%).

[V(O)(oda)(μ-OMe)]$_2$[K(H_2O)]$_2$ 2b. Following an analogous synthetic procedure as described above, starting from **1** but using finely powdered solid KOH as reactant, compound **2b** was obtained as blue crystals (90% yield). IR (KBr/cm^{-1}): 3429 s br ν(OH), 1640 s very br ν(COO asymm), 1399 s br ν(COO symm), 1100 s ν(COC asymm), 989 s ν(VO). μ_{eff} (solid state) = 2.21 μ_B. (Found: C, 21.68; H, 2.54. $C_{10}H_{16}O_{15}K_2V_2$ requires C, 21.58; H, 2.87%).

Interaction of complex 1 with N-donor bases: synthesis of compounds 2c–2g containing the anion [V(O)(oda)(μ-OMe)]$_2^{2-}$. A general procedure for the synthesis of these compounds is as follows: Onto a solution of **1** (0.235 g, 1 mmol) in MeOH (5 ml) was added the N-donor base (2 mmol). The solution colour became dark blue and the mixture was stirred for 1 hour. Volatiles were removed and the solid residue was washed with acetone. Crystallization was from methanol, in which the compounds are moderately soluble.

[V(O)(oda)(μ-OMe)]$_2$[H(2-Mepy)]$_2$·H_2O **2c**. Dark blue crystalline solid (80% yield). IR (KBr/cm^{-1}): 3424 s br ν(OH), 2831 m ν(NH$^+$), 1645 s very br ν(COO asymm), 1403 s ν(COO symm), 1084 s ν(COC asymm), 975 s ν(VO). μ_{eff} (solid state) = 2.33 μ_B. (Found: C, 40.00; H, 4.49; N, 4.19. $C_{22}H_{32}O_{15}N_2V_2$ requires C, 39.64; H, 4.80; N, 4.20%).

[V(O)(oda)(μ-OMe)]$_2$[H(2,6-Me$_2$py)]$_2$ **2d**. Dark blue microcrystalline solid (80% yield). IR (KBr/cm^{-1}): 1666 s br ν(COO asymm), 1399 s ν(COO symm), 1096 s ν(COC asymm), 990 s ν(VO). μ_{eff} (solid state) = 2.43 μ_B. (Found: C, 42.41; H, 4.92; N, 4.17. $C_{24}H_{34}O_{14}N_2V_2$ requires C, 42.60; H, 5.03; N, 4.14%).

[V(O)(oda)(μ-OMe)]$_2$[H(4-Me$_2$Npy)]$_2$ **2e**. Dark microcrystalline blue solid (70% yield). IR (KBr/cm^{-1}): 1662 s br ν(COO asymm), 1403 s ν(COO symm), 1084 s ν(COC asymm), 981 s ν(VO). μ_{eff} (solid state) = 2.30 μ_B. (Found: C, 40.79; H, 5.05; N, 8.12. $C_{24}H_{36}O_{14}N_4V_2$ requires C, 40.79; H, 5.10; N, 7.93%).

[V(O)(oda)(μ-OMe)]$_2$[HNEt$_3$]$_2$·H_2O **2f**. Blue solid (64% yield). IR (KBr/cm^{-1}): 3422 br ν(OH), 2936, 2676 s ν(NH$^+$), 1628 s br ν(COO asymm), 1398 s ν(COO symm), 1098 s ν(COC asymm), 986 s ν(VO). μ_{eff} (solid state) = 2.16 μ_B. (Found: C, 38.82; H, 6.90; N, 4.25. $C_{22}H_{48}O_{15}N_2V_2$ requires C, 38.71; H, 7.04; N, 4.11%).

[V(O)(oda)(μ-OMe)]$_2$[PhNH$_3$]$_2$·½H_2O **2g**. Blue solid (67% yield). IR (KBr/cm^{-1}): 3434 br ν(OH), 2932, 2642 br ν(NH$^+$), 1620 s br ν(COO asymm), 1380 s ν(COO symm), 1090 s ν(COC asymm), 990 s ν(VO). μ_{eff} (solid state) = 2.16 μ_B. (Found: C, 39.75; H, 4.23; N, 4.35. $C_{22}H_{31}O_{14.5}N_2V_2$ requires C, 40.18; H, 4.73; N, 4.26%).

Reaction of complex 1 with pyridine: [V(O)(oda)(py)$_2$] 3. A solution of **1** (0.118 g, 0.5 mmol) in methanol (5 ml) was reacted with an excess of pyridine (1 ml). The deep blue solution was stirred at room temperature for 5 h. Volatiles were removed and the oily residue was washed with petroleum ether. Complex **3** was obtained as a deep blue solid, which was additionally washed with acetone and Et_2O and dried *in vacuo* (75%). IR (KBr/cm^{-1}): 1666 s br ν(COO asymm), 1399 s br ν(COO symm), 1112 s ν(COC asymm), 974 s ν(VO). μ_{eff} (solid state) = 1.71 μ_B. (Found: C, 46.68; H, 3.71; N, 7.84. $C_{14}H_{14}O_6N_2V$ requires C, 47.06; H, 3.92; N, 7.81%).

Table 5 Crystallographic data for complexes **1**, **2a** and **4**

	1	**2a**	**4**
Formula	$C_4H_8O_8V$	$C_{10}H_{18}O_{16}Na_2V_2$	$C_{28}H_{28}N_4O_{14}V_2$
M	235.04	546.14	746.42
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Aba*2 (no. 41)	*Cmc*21 (no. 36)	$P2_1/a$ (no. 14)
a/Å	8.919(3)	15.884(8)	15.995(5)
b/Å	10.889(2)	6.860(4)	10.784(5)
c/Å	8.593(3)	18.394(6)	19.143(5)
β/°	—	—	114.01(5)
$V/Å^3$	834.5(4)	2004.3(17)	3016.3(16)
Z	4	4	4
D_c/g cm^{-3}	1.871	1.783	1.644
μ(Mo-K$_\alpha$)/mm^{-1}	1.204	1.053	0.699
F(000)	476	1080	1528
Unique reflections, $I \geq 2\sigma(I)$	399	1053	4321
R	0.024	0.067	0.071
wR	0.065	0.160	0.172

[V(O)(oda)(bipy)]·H_2O 4. Onto a stirred solution of **1** (0.235 g, 1 mmol) in MeOH (10 ml) was added bipy (0.176 g, 1 mmol). Compound [V(O)(oda)(bipy)] was immediately precipitated as a yellow microcrystalline solid (0.32 g, 80%). Good quality crystals of **4** were obtained by recrystallization from hot water. IR (KBr/cm^{-1}): 3551–3422 br *ν*(OH), 1666 s br *ν*(COO asymm), 994 s *ν*(VO). μ_{eff} (solid state) = 1.67 μ_B. (Found: C, 45.44; H, 3.77; N, 7.52. $C_{14}H_{14}O_7N_2V$ requires C, 45.04; H, 3.75; N, 7.51%).

[V(O)(oda)(phen)]·H_2O 5. A water solution (2 ml) of *o*-phen·HCl (0.185 g, 0.8 mmol) was slowly added to an aqueous solution (5 ml) of **1** (0.185 g, 0.8 mmol). The resulting mixture was left to stand for 4 days. After that, complex **5** was obtained as well formed green crystals (0.173 g, 53%). IR (KBr/cm^{-1}): 3556–3369 br *ν*(OH), 1678 s br *ν*(COO asymm), 999 s *ν*(VO). μ_{eff} (solid state) = 1.63 μ_B. (Found: C, 48.84; H, 3.50; N, 7.44. $C_{14}H_{14}O_7N_2V$ requires C, 48.36; H, 3.53; N, 7.05%).

Crystallography

A summary of the fundamental crystal and refinement data is given in Table 5. Well-formed crystals of **1** (blue), **2a** (deep blue) and **4** (yellow) were mounted on a Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å). In all cases, the cell dimensions were refined by least-squares refinement of 25 reflections in the 2*θ* range of 10–20°. The intensity data were corrected for Lorentz and polarization effects. In any case, three standard reflections were monitored every two hours during data collection and minimum decay was observed. In the case of compound **1**, no absorption correction was applied in view of the tiny size of the crystals. Atomic scattering factors are those reported by Cromer and Waber.[31] Structure solutions were carried out by direct methods using the SIR-97[32] package of programs. Refinements were made by full matrix least squares on all F^2 data using SHELXL-97.[33] Generally, the hydrogen atoms bound to carbon were introduced at calculated positions (C–H = 0.95 Å) in the later stages of refinement, while those of the water molecules were found from Δ*F* maps. Only for compound **2a** could these hydrogen atoms not be located. Also because of the limited number of reflections available for **2a**, its carbon atoms were allotted isotropic thermal parameters. In any other case, the anisotropic model was used for the non-hydrogen atoms. The H atoms bound to carbon atoms were treated with the riding model, whereas those of the H_2O molecules were fully refined. For compound **4**, however, the O_w–H distances were constrained to the value of 0.90 Å and the H–O_w–H angle to 106°. No unusual trend in Δ*F* *vs.* F_o or (sin*θ*)/*λ* was observed. Final difference syntheses showed no significant electron density residues. The molecular drawings were made using the program ORTEP-III for Windows.[34] All the computational work was performed by using the user-friendly graphic interface of WINGX.[35]

CCDC reference numbers 202077–202079.

See http://www.rsc.org/suppdata/dt/b3/b300914a/ for crystallographic data in CIF or other electronic format.

Computational details

The electronic structure and geometries of [V(O)(oda)(H_2O)$_2$] **1** and the alternative isomer of **1** with a *fac* coordination for the oda ligand were computed within the density functional theory at the unrestricted B3LYP[36] level, using the LANL2DZ basis set.[37] A set of d polarization functions was added to C and O atoms. The optimized geometries were characterized as local energy minima by diagonalization of the analytically computed Hessian (vibrational frequency calculations). All the calculations were performed using the Gaussian 98 suite of programs.[38] Cartesian coordinates for the optimized molecules are available from the authors upon request.

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