

www.elsevier.nl/locate/poly

Polyhedron 19 (2000) 2003-2010



Ligand reactivity, substituent effects and solvent interactions in the spectra and structure of some oxovanadium(V) chelates with Schiff bases. Proof for dimeric species

Chris Tsiamis *, Byron Voulgaropoulos, Dimitrios Charistos, George P. Voutsas, Constantin A. Kavounis

Department of Chemistry and Department of Physics, University of Thessaloniki, 54006 Thessaloniki, Greece

Received 29 September 1999; accepted 9 June 2000

Abstract

The reaction of bis(β -dionato)oxovanadium(IV) chelates, VO β_2 , with substituted benzoylhydrazines, XbH₂, was explored in alcoholic solutions and oxovanadium(V) compounds with Schiff bases as ligands were obtained in high yield. These VOL(OR) compounds have alkoxide as coligand and the asymmetic tridentate Schiff base ligands, L²⁻, bind to the oxovanadium core through the carbonyl oxygens and the imine nitrogen. Substituents attached to benzoylhydrazines affect the electron density about the oxovanadium core. While electron attracting substituents appear to favour monomeric square pyramidal chelates, the derivatives having electron repelling groups seem to encourage formation of dimeric structures and alkoxo bridged dimers are obtained. The crystal structures of the products of the reaction of bis(1-phenyl-1,3-butanedionato)oxovanadium(IV), VO(bzac)₂, with *o*-nitrobenzoylhydrazine (*o*-O₂NbH₂) and *m*-methoxybenzoylhydrazine (*m*-CH₃ObH₂) that are reported demonstrate the influence of the substituents as well as the role of the solvent. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Alkoxo compounds of oxovanadium(V); Crystal structure of compounds of oxovanadium(V); Hydrazonato compounds of oxovanadium(V); Oxovanadium(V); Oxovanadium(V); dimers; Reactivity of bis(β-dionato)oxovanadium(IV) chelates; Hydrazonato tridentate Schiff base ligands

1. Introduction

Vanadium exists in a plethora of oxidation states and its coordination compounds play an important role in nitrogen activation and fixation and other biologically important reactions [1–3]. This revelation has stimulated interest in the stereochemistry and reactivity of its coordination compounds that contain the diazo and hydrazido group because they may provide some understanding of the mechanism of metalloenzymatic reduction of dinitrogen. Substituted aroylhydrazones possessing a suitably disposed amino group, whilst often bind directly to the metal [4], they may also interact with compounds containing carbonyl groups, for example salicylaldehydes and β -diones [5–10]. Such reactions have been exploited adroitly to form Schiff

bases that are capable of confining metal atoms and controlling their properties and functionality [11]. Regarding β -diones and the oxovanadium(IV) core, the 1-phenyl-1,3-propanedione [6–9] has been gainfully employed in studies involving the Schiff bases resulting from the condensation reaction with aroylhydrazines [4-9]. Recent studies have indicated that solvent interactions with the moieties resulting from the ligation of such tridentate Schiff bases to the oxovanadium(IV) core have significant repercussions on the structure of the resulting chelates since solvent molecules or solvent fragments participate as coligands [6-9]. Other β diones have not been utilised in similar studies, even though seemingly minor changes in ligand structure incurred by groups within the β -dionato moiety have a profound effect on the stereochemistry, the spacing of the energy levels, the redox potentials and other distinctive physicochemical properties of the β -dionato chelates [12]. The effects of substituents attached to the phenyl ring of benzoylhydrazines on the electron distri-

^{*} Corresponding author. Tel.: + 30-31-997-863; fax: + 30-31-427-218.

E-mail address: tsiamis@chem.auth.gr (C. Tsiamis).

bution of the Schiff bases have not been explored sufficiently. Further, the reactivity of the $bis(\beta$ -dionato)oxovanadium(IV) chelates, $VO\beta_2$, has not been probed adequately in the preparation of tridentate Schiff base ligands, even though the $VO\beta_2$ chelates have been engaged successfully in ligand addition and ligand exchange reactions and are often used as starting material in syntheses [13,14].

This investigation was undertaken in order to explore the reactivity of certain bis(β-dionato)oxovanadium(IV) chelates with aroylhydrazines, to assess the influence of the reaction medium in the formation of products, to appraise the effect of substituents in the structure and the spectroscopic properties of the chelates formed, to assay the possibility of oxygen bridge creation and formation dimeric structures and to determine the stereochemistry of the resulting compounds. In this work the preparation of some β -dionate(benzoyl)hydrazonato(2-)oxovanadium(V) chelates is reported, the structures of [ethoxo(4-phenyl-2,4-butanedione(2'-nitrobenzoyl)hydrazonato(2-))oxo-vanadium(V)] and the anticoplanar bis $[\mu_2$ -methoxo(4-phenyl-2,4-butanedione(3'methoxybenzoyl)hydrazonato(2-))oxovanadium(V)] are described and the results of the investigation are presented and discussed.

2. Experimental

2.1. Preparation and characterisation of the $VO(\beta bh)OR$ compounds

The β -diones, β H, namely 2,4-pentanedione (acetylacetone, acacH), 1-phenyl-1,3-butanedione (benzoylacetone, bzacH), 1-phenyl-4,4,4-trifluoro-1,3-butanedione (trifluorobenzoylacetone, bztfH) and 1-thenyl-4,4.4-trifluoro-1,3-butanedione (trifluorothenoylacetone, thtfH), were purchased from Sigma–Aldrich. The bis(β -dionato)oxovanadium(IV) chelates (VO β_2), that were used as starting materials, were prepared and purified as described in the literature [15,16]. The compound (n-C₄H₉)₄NVO₃ was prepared by established procedures [17]. The substituted aroylhydrazines, XbhH₂, were procured from Fluka. Certain Schiff bases resulting from the reaction of benzoylacetone or trifluorobenzoylacetone with substituted benzoylhydrazines were prepared by literature methods [18] and characterised. The synthesis of the new vanadium chelates was accomplished as follows:

In a 200 cm³ conical flask containing a magnetic follower are placed 10 mmol of $VO\beta_2$ and ~ 80 cm³ alcohol and the mixture is stirred at ambient temperature until complete dissolution. Then 20 mmol of aroyl-hydrazine (also dissolved in the same alcohol) are added while stirring and the colour of the reaction mixture changes from brown to red-brown. The stirring continued for an additional 20 h. The VO(Xbh)OR compounds precipitated as red-brown solids. Recrystallisation was achieved by redissolving the solid in alcohol and allowing crystals to grow under refrigeration.

The chelates prepared, their stoichiometry and melting points are given in Table 1.

2.2. X-ray crystallographic analysis of $[VO(o-O_2Nbhbzac)OC_2H_5]$ and of $[VO(m-CH_3Obhbzac)(\mu_2-OCH_3)]_2$

Intensities of X-ray reflections within two octants of the reciprocal sphere were collected by means of a four-circle Philips-STOE computer-controlled X-ray diffractometer employing graphite-filtered Mo K α radiation. The orientation matrix and refined unit cell dimensions of the crystal of [ethoxo(4-phenyl-2,4-

Table 1

Elemental analyses and physicochemical data of some aroylhydrazonato(2-)oxovanadium(V) chelates containing alkoxo ligands, VOL(OR)

	Compound	Yield (%)	M.p. (°C) ^a	C (%)	H (%)	N (%)
1	VO(p-NO ₂ bhacac)OMe	73	131d	43.7 (43.47)	3.93 (3.93)	11.4 (11.70)
2	VO(p-NO ₂ bhacac)OEt	77	153d	44.7 (45.05)	4.27 (4.32)	11.8 (12.26)
3	VO(p-NO ₂ bhacac)OCHMe ₂	91	251d	46.7 (46.49)	4.72 (4.68)	11.1 (10.84)
4	VO(p-NO ₂ bhbzac)OMe	95	180d	51.3 (51.32)	3.79 (3.83)	9.87 (9.97)
5	VO(p-NO ₂ bhbzac)OEt	83	210d	52.3 (52.42)	4.20 (4.17)	9.75 (9.65)
6	VO(p-NO ₂ bhbzac)OCHMe ₂	87	180d	53.8 (53.46)	4.52 (4.49)	9.47 (9.35)
7	VO(o-NO ₂ bhbzac)OMe	93	207d	51.1 (51.32)	3.86 (3.83)	10.2 (9.97)
8	VO(o-NO ₂ bhbzac)OEt	90	180d	51.9 (52.42)	4.21 (4.17)	9.57 (9.65)
9	VO(o-NO ₂ bhbzac)OCHMe ₂	82	202d	53.2 (53.46)	4.37 (4.49)	9.29 (9.35)
10	VO(p-NO ₂ bhbztf)OCHMe ₂	81	177d	47.7 (47.73)	3.37 (3.40)	8.39 (8.35)
11	VO(p-NO ₂ bhthtf)OEt	71	230d	41.3 (41.22)	2.68 (2.65)	8.44 (8.48)
12	VO(p-NO ₂ bhthtf)OCHMe ₂	74	184d	42.4 (42.45)	3.01 (2.97)	8.28 (8.25)
13	[VO(m-CH ₃ Obhbzac)OMe] ₂	91	219d	55.8 (56.17)	4.71 (4.71)	6.84 (6.89)
14	$[VO(m-CH_3Obhthtf)OMe]_2$	81	185d	44.1 (43.79)	3.01 (3.03)	5.94 (6.01)

^a d, decomposition.

Table 2

Crystal data and experimental details for the structural study of (a) $[VO(o-O_2Nbhbzac)OC_2H_5]$ and (b) $[VO(m-CH_3Obhbzac)(\mu_2-OCH_3)]_2$

Formula mass, $M_{\rm r}$	(a) $C_{19}H_{18}N_3O_6V$ 435.31	(b) C ₁₉ H ₁₉ N ₂ O ₅ V 406.31
Crystal parameters		
Crystal shape	dark brown plates	deep brown rectangular prisms
Crystal size (mm)	$0.75 \times 0.45 \times 0.25$	$0.70 \times 0.55 \times 0.32$
Crystal system	monoclinic	triclinic
Space group	$P2_{1}/n$	$P\overline{1}$
Unit-cell dimensions		
a (Å)	11.033(5)	7.550(3)
$b(\mathbf{A})$	7.537(5)	10.010(3)
$c(\dot{A})$	23.369(9)	13.637(5)
α (°)	90.00	106 99(2)
β (°)	93 920(5)	92 76(2)
γ (°)	90.00	105 70(3)
$V_{\rm e}$ (Å ³)	1938.7(16)	939.8(6)
Units per cell. Z	4	2
D_{calc} (Mg m ⁻³)	1.4914(12)	1.43548(9)
Measurement of intensity	data	
Instrument	PW100-STOE	
Radiation (Å)	Mo K α , $\lambda = 0.71069$	
Temperature (K)	298(2)	
Monochromometer	Graphite	
Scan mode	$\omega - 2\theta$	
θ Range (°)	1.76-27.57	1.58-30.00
Linear absorption	1 097	1 14
coefficient μ (mm ⁻¹)		
Reflections measured	4233	4728
Independent reflections	3825	4671
Reflections observed	2647	3454
$(I > 2\sigma(I))$	2017	5151
Indices limits		
h	-14-9	-10-5
k	0_9	-14-13
l	0-30	0–19
Refinement and final discr	epancy factors	
Refinement	full-matrix	full-matrix
	least-squares on	least-squares on F^2
	F^2	
Parameters refined	323	301
Largest difference peak	0.399, -0.397	0.351, -0.416
and hole (e A^{-3})		
$R = \Sigma(F_{\rm o} - F_{\rm c}) / \Sigma F_{\rm o} $	0.0512	0.0387
$R_{w} = [\Sigma w (F_{o} - F_{c})^{2} / $	0.0777	0.1026
$\Sigma w(F_{\rm o})^2]^{1/2}$		

butanedione(2'-nitrobenzoyl)hydrazonato(2-))oxovanadium(V)], [VO(o-O₂Nbhbzac)OC₂H₅] and of bis[μ_2 methoxo(4-phenyl-2,4-butanedione(3'-methoxybenzoyl)hydrazonato(2-))oxovanadium(V)], [VO(m-CH₃Obhbzac)(μ_2 -OCH₃)], were obtained from independent reflections of high intensity ($12 \le \theta \le 15^\circ$). Details of crystal analysis, data collection and structure refinement are given in Table 2, together with the final values for the unit cells. All intensities were corrected as usual for Lorentz and polarization effects. In view of the low μ value no correction for absorption deemed necessary. In both cases the vanadium position was deduced by direct methods employing the SHELXS-86 and the SIR-97 programs [19,20] and used to compute a first-approximation electron-density synthesis, which revealed the position of all remaining atoms except the hydrogens. After least-squares refinements with the non-hydrogen atoms, the hydrogen atoms were also located in the difference Fourier map using the SHELX-97 program [21]. The figures of the clinographic projection were produced with the DIAMOND and ATOMS programs [22]. Refinement was carried out by full-matrix least-squares, with unit weight to all reflections.

3. Results and discussion

Many oxometallates undergo condensation reactions in which polyatomic groups replace the oxygen ligand. For example, the diazenido and the hydrazido groups are attached to molybdenum by employing oxomolybdenum compounds as precursors [23]. In the case of $bis(\beta$ -dionato)oxovanadium(IV) chelates, the mixing of alcoholic solutions of $VO\beta_2$ and a substituted benzoylhydrazine, XbhH₂, is accompanied by a change in colour (suggesting commencement of a reaction) and formation of a precipitate as the main product. The elemental analysis of the recrystallised precipitate revealed the presence of nitrogen while the stoichiometry disclosed dependence on the alcohol employed as solvent. Interestingly, the yield is maximised when the metal-to-benzoylhydrazine molecule is 1:2 and the reaction mixture is accessible to atmospheric oxygen. Further, in a series of reactions using the same alcohol as solvent and the same XbhH₂ but different chelate $VO\beta_2$, the composition of the main product suggested abstraction of a β -ketoenol and entrapment of a aroylhydrazine molecule by the vanadium atom. The diamagnetic behaviour of the new compounds indicated absence of unpaired electrons while the lack of absorption in the electronic excitation spectra at wavenumber below $\sim 2.50 \ \mu m^{-1}$ reaffirmed the absence of electrons localised in the d orbital manifold [12,13]. These observations suggested an oxidative displacement reaction in the oxovanadium core converting the metal to vanadium(V) with sacrificial species one of the ligated β -dionato anions and formation of chelates corresponding to the general formula VOL(OR), where OR^{-} is an alkoxide and L^{2-} denotes the Schiff base resulting from the partial addition-elimination reaction of the β-dionato anion with an aroylhydrazine. To verify this hypothesis, aroylhydrazones and either 1-phenyl-1,3-butanedione (bzacH) or trifluorobenzoylacetone (bztfH) were employed to obtain Schiff bases which were subsequently

reacted with $(n-C_4H_9)_4NVO_3$ to produce chelates. The later reaction afforded products identical to those obtained by the reaction of the appropriate VO β_2 chelates with aroylhydrazines. Interestingly the yield of the onepot synthesis was appreciably higher. Further information regarding the structure of the new compounds was acquired from their electronic absorption spectra.

3.1. Electronic excitation spectra

In the electronic excitation spectra of the VOL(OR) chelates no absorptions attributable to the ligand field excitations happen. The lack of paramagnetic interactions and the absence of ligand field transitions indicate oxidation of the metal to vanadium(V) and disallow any inference about the ordering of the d orbitals. A strong broad band (or envelope) is observed at ~ 2.50 μ m⁻¹ and is solvent depended. The absorption in this region, for energy and intensity reasons, should be attributed to a charge transfer excitation most likely from a π ligand orbital to the manifold of the d metal orbitals. The influence of the solvent in this band is clearly evident in the spectra of the monomers in which shifts and alterations of band shape are notable upon change of solvent. Actually in the spectra of the monomers obtained from 1,2-dichloroethane solutions this LMCT excitation affords an envelope with no definite maximum. From the shape of the envelope and the preliminary analysis the occurrence of a band with maximum at $\sim 2.0 \ \mu m^{-1}$ is deduced. In the spectra of the monomers obtained employing acetonitrile or DMSO as solvent, a well-formed band is evident at $\sim 2.3 \ \mu m^{-1}$. This shift suggests change of the ordering of the d orbitals effected by the occupation of the vacant coordination site. Further information regarding bonding in the chelates under consideration were sought from the infrared spectra.

3.2. Infrared spectra

In the IR spectra of the compounds resulting from the reaction of the substituted benzoylhydrazines with bis(β -dionato)oxovanadium(IV) chelates, the absence of absorptions above 3100 cm^{-1} implied that the hydrazino group, -NHNH₂, has taken part in an additionelimination reaction and that proton transfer has taken place. The marginal shift in the diminished band that turns out at $\sim 1578 + 10$ cm⁻¹ and is associated with the stretching vibration of a carbonyl group of the β -dionato anion [13] suggested that carbonyl oxygen remains bonded to vanadium since the C-O bending mode appears as a rather strong band around 1160 cm⁻¹. Further, the intense band occurring at $\sim 970 \pm$ 30 cm^{-1} and assigned to the V=O stretching vibration [23-25] indicated that the V=O core stays intact, while the variation in frequency to the V=O stretching vibration suggests that the $d_{\pi}-p_{\pi}$ overlap between the vanadium and the oxygen atoms is influenced by the substituents and the coligands. The implication of these observations is that the condensation reaction of hydrazine does not involve the oxo ligand. Further, it transpires that while one of the β -dionato anions, β^- , participates in the condensation reaction, the other becomes the sacrificial species of the oxidative displacement reaction.

In addition to IR absorptions originating from V=O core and the β -dione fragment of the Schiff base, the bands may be distinguished in those arising from the entrapped hydrazine species and in those emerging from the alkoxy group. The presence of substituents attached to the β -dionato moiety and the existence of groups appended to the phenyl ring of the aroylhydrazine engender absorption bands and spectral shifts. Whenever the β -diones employed are non-symmetric the site of the attack becomes important. In the case of bzac⁻ the phenyl ring renders the adjacent carbonyl group immune to the attack while in (bztf⁻) the strong electron attracting ability of the trifluoro group ensures that the attack is targeted in the carbonyl neighbouring the phenyl ring. In the ensuing Schiff bases, the =NH proton is prone to form intermolecular and intramolecular hydrogen bonds as the bands observed at ~ 3400 (broad) and 1630 cm^{-1} indicated. These bands are not present whenever the $bis(\beta$ -dionato)oxovanadium(IV) is employed, as the β -dione source and the chelates are obtained in the one-pot synthesis. In the chelates prepared the intense absorption observed at $\sim 1600 \pm 10$ cm^{-1} probably emanates from the azomethine (C=N) stretching mode [26] while the high intensity band occurring at $\sim 1520 \pm 15$ cm⁻¹ and is tentatively assigned to the $>C=N-N=CPhO(^{-})$ entity indidelocalisation. The cates extensive prototropic >C=NNHCOPh entity in the Schiff base apparently undergoes hydrogen abstraction from the tautomeric form, >C=N-N=C(OH)Ph, to produce the electronrich hydrazido(2-) species because no band could be associated with vibrations of either the N-H or the O-H bonds. The process of hydrogen abstraction is accomplished presumably with the aid of atmospheric oxygen that facilitates the oxidation of the metal to vanadium(V). Taking into consideration the strongly electron-attracting nature of the metal and the availability of electron density at the nitrogen atoms the wholly reasonable assumption may be made that they may be involved in bonding interactions. On the basis of previous structural data and the geometry of the resulting Schiff base, the nitrogen atom engaged in the condensation reaction is presumed to be bonded to the metal atom. This assumption is further supported by the relatively weak bands at around 475 ± 10 cm⁻¹ that are assigned to the stretching vibrations of the V-N bonds [27]. The stretching vibrations of the V-O

Table 3										
Selected	interatomic	distances	(Å)	and	bond	angles	(°) of	f [VO(o-NO	,bhbzac)OC	2H5]

V-O(1)	1.580(2)	N(1)–N(2)	1.394(3)	C(8)–C(9)	1.374(5)
V-O(4)	1.758(2)	N(2)-C(2)	1.327(3)	C(9)–C(10)	1.380(5)
V-O(2)	1.860(2)	N(3)-C(13)	1.461(4)	C(11)-C(12)	1.475(4)
V-O(3)	1.915(2)	C(1)–C(2)	1.493(4)	C(12)–C(13)	1.391(4)
V-N(2)	2.061(2)	C(4)–C(5)	1.475(4)	C(12)-C(17)	1.393(4)
O(2)–C(4)	1.324(3)	C(2)–C(3)	1.401(4)	C(13)–C(14)	1.391(4)
O(3)-C(11)	1.318(3)	C(3)–C(4)	1.367(4)	C(14)-C(15)	1.368(5)
O(5)–N(3)	1.216(3)	C(5)-C(10)	1.391(4)	C(15)-C(16)	1.379(5)
O(6)–N(3)	1.225(3)	C(5)–C(6)	1.396(4)	C(16)–C(17)	1.373(5)
O(6)-C(18)	1.453(5)	C(6)-C(7)	1.366(5)	C(18)–C(19)	1.442(6)
N(1)-C(11)	1.286(3)	C(7)–C(8)	1.384(5)		
O(1)-V-O(4)	106.05(11)	O(5)-N(3)-O(6)	124.2(3)	C(10)-C(9)-C(8)	120.6(3)
O(1)-V-O(2)	107.15(10)	O(5)-N(3)-C(13)	118.0(2)	C(9)–C(10)–C(5)	120.5(3)
O(4)-V-O(2)	95.94(9)	O(6)-N(3)-C(13)	117.7(2)	N(1)-C(11)-O(3)	121.7(2)
O(1)-V-O(3)	107.96(10)	O(2)-C(4)-C(3)	120.8(3)	N(1)-C(11)-C(12)	119.1(2)
O(4)-V-O(3)	89.71(9)	O(2)-C(4)-C(5)	115.8(2)	O(3)-C(11)-C(12)	119.2(2)
O(2)-V-O(3)	141.26(10)	C(3)-C(4)-C(5)	123.3(3)	C(13)-C(12)-C(17)	116.5(3)
O(1)-V-N(2)	99.99(9)	C(4)-C(3)-C(2)	124.6(3)	C(13)-C(12)-C(11)	123.6(2)
O(4)-V-N(2)	152.86(10)	N(2)-C(2)-C(3)	120.9(2)	C(17)-C(12)-C(11)	119.8(3)
O(2)-V-N(2)	83.40(9)	N(2)-C(2)-C(1)	120.2(2)	C(16)-C(17)-C(12)	121.5(3)
O(3)-V-N(2)	74.90(9)	C(3)-C(2)-C(1)	118.9(2)	C(15)-C(14)-C(13)	118.7(3)
C(4)–O(2)–V	133.94(18)	C(10)-C(5)-C(6)	118.0(3)	C(14)-C(15)-C(16)	120.5(3)
C(11)–O(3)–V	117.74(16)	C(10)-C(5)-C(4)	120.3(3)	C(15)-C(16)-C(17)	120.4(4)
C(18)–O(4)–V	124.6(2)	C(6)-C(5)-C(4)	121.7(3)	C(14)-C(13)-C(12)	122.4(3)
C(11)–N(1)–N(2)	108.1(2)	C(7)-C(6)-C(5)	121.2(3)	C(14)-C(13)-N(3)	117.0(3)
C(2)-N(2)-N(1)	115.5(2)	C(6)-C(7)-C(8)	120.2(4)	C(12)-C(17)-N(3)	120.4(2)
C(2)–N(2)–V N(1)–N(2)–V	128.24(18) 116.25(17)	C(9)-C(8)-C(7)	119.5(3)	O(4)-C(18)-C(19)	109.6(4)

bonds appear as rather medium intensity bands around 525 ± 20 cm⁻¹. Some of the metal-ligand absorptions are not related to the Schiff base and are solvent dependent. For instance, in the IR spectra of the product of the reaction of *m*-methoxybenzoylhydrazine with $VO\beta_2$ in methanol a very broad feature centred around 340 cm⁻¹ propounded the possibility of additional metal-oxygen bonds and suggested the likely occurrence of dimeric structures [27]. The broad feature appears to consist of a number of overlapping peaks attributable to deformations of bridging V-O-V bonds and vibrational coupling of low frequency modes that complicate the assignments in this region. The notion of the existence of dimeric structures was enhanced by the shift of the bands due to the C-O vibrations to higher wave-numbers by 10-30 cm⁻¹ that suggested absence of additional bonding interactions of the carbonyl oxygens. The oxo ligand was not implicated in the formation of the dimeric species, because the shift of the band due to the V=O stretching vibration was imperceptible [23–25]. Since neither the infrared spectra nor the elemental analyses revealed the presence of water molecules, the alkoxo groups were implicated in the formation of dimeric species. Confirmation of their existence and details of the structures of representative compounds of the new chelates were acquired from the X-ray diffraction study.

3.3. Description of the structures

The X-ray diffraction study of [ethoxo(4-phenyl-2,4dione(2' - nitrobenzoyl)hydrazonato(2 -)oxovanadium-(V)], $[VO(o-NO_2bhbzac)OC_2H_5]$, disclosed that in the unit cell there are four vanadium atoms. The positional parameters, the interatomic distances and the bond angles (Table 3) reveal that the coordination environment in which the vanadium atoms exist is approximately square pyramidal with the oxo ligand engaging the apical position. The oxygen of the ethoxy group, the carbonyl oxygens and the nitrogen of the primary amino group that reacted with the β -dione, are in the immediate vicinity of vanadium. While the aforementioned oxygen and nitrogen atoms are virtually in the same plane (the basal plane), the central atom is above the basal plane by 0.480(2) Å and is directed towards the oxo ligand. The V-Ooxo interatomic distance at 1.580(2) Å is in accord with other pentacoordinate oxovanadium compounds (Table 4). These data reaffirm the indications of coordination unsaturation suggested by the solvent shifts in the electronic excitation spectra. The Schiff base ligand forms a six-membered and a five-membered chelate ring and the interatomic distances within the C(2)-N(2)-N(1)-C(11)group reassert that no hydrogen is bonded to the nitrogen atoms and that extensive electron delocalisation has taken place. The planar aromatic rings form a dihedral angle of $34.53(5)^\circ$. A clinographic projection of $[VO(o-NO_2bhbzac)OC_2H_5]$ and its labelling scheme is shown in Fig. 1.

The X-ray diffraction study of bis[µ2-methoxo-(4 - phenyl - 2,4 - dione(3' - methoxybenzoyl)hydrazonato-(2-))oxovanadium(V)], $[VO(m-CH_3Obhbzac)OCH_3]_2,$ disclosed that in the unit cell there are only two vanadium atoms. The positional parameters (Table 4) show that the coordination environment in which the vanadium atoms exist resembles closely that of the metal in $[VO(o-NO_2bhbzac)OC_2H_5]$ and other [VO(L)OR]chelates. The vanadium atoms are separated by a distance of only 3.370(2) Å, suggesting the possibility of a dimeric structure. The oxo ligand binds to one vanadium atom but exists at a distance of 4.750(2) A from the other vanadium centre, implying absence of bonding interactions. However, at a distance of 2.360(2) Å from the vanadium centre the position *trans* to the oxo ligand is engaged by the oxygen of another alkoxo ligand. The methoxo group is strongly ligated to one vanadium centre and interacts with the other forming a bridge. The resulting distorted octahedral structures of the oxovanadium centres are bridged by one shared edge leading to the creation of a $\{VO(\mu_2-OR)_2VO\}^{4+}$ core. As the oxygen atom of the alkoxo group becomes involved in covalent interactions with the other vanadium atom, the V-O_{alkox} distance increases and the change in electron density should affect the interactions of the nitrogen atom in trans position. A diminution of



Fig. 1. A clinographic projection and labelling scheme of [ethoxo(4-phenyl - 2,4 - butanedione(2' - nitrobenzoyl)hydrazonato(2 -))oxovanadium(V)]. The ATOMS drawing shows the thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

the distance of the nitrogen atom in *trans* position from the vanadium centre is envisaged and, indeed, such a trend becomes apparent when the interatomic distances listed in Table 5 are considered. The compounds described in this work do not follow exactly the expected trend.

In the binuclear compound $[VO(m-CH_3Obhbzac)-OCH_3]_2$, the $\{VO(\mu_2-OR)_2VO\}^{4+}$ core forms a parallelepiped and the mutual steric requirements of the

Table 4 Bond lengths in some oxovanadium chelates with tridentate Schiff bases and other ligands

Compound ^c	V–O _{oxo}	V–N	$V - O_{\beta}$	V–O _h	V–O _{alk} ^a	V–O ^b	N–N	V…V	Ref.
[VO(bhbzac)OC ₂ H ₅]	1.595(3)	2.070(3)	1.848(2)	1.907(2)	1.750(3)		1.400(6)		[7]
[VO ₂ (bzacGRP)]	1.601(3)	2.133(4)	1.929(4)	1.980(4)	1.616(3)		1.405(5)		[9]
[VO(bhbzac)O(CH ₂) ₂ OH]	1.583(4)	2.093(4)	1.883(3)	1.937(3)	1.789(3)	2.286(3)	1.408(5)		[10]
[VO(<i>m</i> -Cl bhbzac)OC ₂ H ₅]	1.598(5)	2.043(6)	1.835(5)	1.893(5)	1.770(4)		1.409(7)		[28]
$[VO(o-O_2Nbhbzac)OC_2H_5]$	1.580(2)	2.061(2)	1.860(2)	1.915(2)	1.758(2)		1.394(3)		This work
[VO(<i>m</i> -CH ₃ Obhbzac)- OCH ₃] ₂	1.584(2)	2.083(2)	1.848(1)	1.922(2)	1.824(2)	2.360(2)	1.396(2)	3.370(2)	This work
$K_4[VO(cit)]_2 \cdot 6H_2O$	1.608(3)		2.022(3)	2.041(3)	2.171(3)	1.977(3)		3.301(3)	[29]
[VO(SalAHE)] ₂	1.619(10)	2.009(11)	1.892(10)	1.985(10)	1.980(9)				[14]
	1.548(9)	2.034(11)	1.888(10)	1.963(10)	1.979(9)			3.068(4)	
{[VO(SalAMHP)] ₂ }O	1.598(4)	2.130(5)	1.880(4)	1.805(4)	1.857(4)				[14]
	1.591(4)	2.115(5)	1.888(4)	1.828(4)	1.759(4)			3.06	
$[VO_2(1,2-pnSal)]_2$	1.619(6)	2.162(5)	1.915(4)	2.120(5) ^{\$}	1.665(4)	2.427(5)		3.222(7)	[30]
[VO ₂ (salGRP)]·CH ₃ OH	1.626(4)	2.143(5)	1.894(4)	1.966(4)	1.635(4)		1.409(7)		[31]
[VO ₂ (salGRT)]	1.611(4)	2.128(3)	1.897(4)	1.996(3)	1.627(3)		1.403(5)		[31]

^a Atoms in the basal position of the alkoxo oxygen.

^b Atoms in the basal position of the oxygen of the aroyl group.

^c bhbzac = 4-phenylbutane-2,4-dionebenzoylhydrazonato(2-); *m*-Clbhbzac = 4-phenylbutane-2,4-dione(*m*-chloro)benzoyl-hydrazonato(2-); cit = citrate; Sal = Salicylaldehyde; GRP and GRT = Girard's reagent P and T, respectively; $H_2SalAHE = 2$ -(salicylideneamino)-1-hydroxyethane; $H_2SalAMHP = 2$ -(salicylideneamino)-1-hydroxypropane; 1,2-pnSal = 1(*N*-salicylideneamino)-2-aminopropane; bzacGRP = 4-phenylbutane-2,4-dione((1-carboxymethyl)pyridinium chloride)hydrazonato(2-); SalGRP = 2-(salicyl(1-carboxymethyl)pyridinium chloride)hydrazonato(2-); SalGRP = 2-(salicyl(1-carboxymethyl)pyridinium chloride)hydrazonato(2-); SalGRP = 2-(salicyl(1-carboxymethyl)pyridinium chloride)-*N*,*N*,*N*-trime-thyl-2-oxo-1-ethanaminium chloride.

Table 5							
Selected interatomic distances	(Å) and	bond a	ngles (°)	of	VO(m-CH ₃	Obhbzac)()	1,-OCH ₃)],

V-O(1)	1.584(2)	N(1)-C(11)	1.295(3)	C(7)–C(8)	1.382(4)
V-O(5)	1.824(2)	N(1)–N(2)	1.396(2)	C(8)–C(9)	1.384(4)
V-O(2)	1.848(1)	N(2)-C(2)	1.315(2)	C(9)–C(10)	1.378(3)
V-O(3)	1.922(2)	C(1)-C(2)	1.496(3)	C(11)–C(12)	1.475(3)
V-N(2)	2.083(2)	C(2)–C(3)	1.419(3)	C(12)-C(13)	1.388(3)
V–O(5) ^a	2.360(2)	C(3)–C(4)	1.362(3)	C(12)-C(17)	1.391(3)
O(2)–C(4)	1.322(2)	C(4)–C(5)	1.472(3)	C(13)-C(14)	1.383(3)
O(3)–C(11)	1.314(2)	C(5)–C(6)	1.399(3)	C(14)-C(15)	1.387(3)
O(4)-C(14)	1.358(3)	C(5)-C(10)	1.401(3)	C(15)-C(16)	1.363(4)
O(4)–C(18)	1.400(4)	C(6)–C(7)	1.377(3)	C(16)-C(17)	1.385(3)
O(5)-C(19)	1.418(3)				
O(1)-V-O(5)	102.43(8)	C(19)-O(5)-V	124.75(15)	C(6)-C(7)-C(8)	120.4(2)
O(1)-V-O(2)	99.69(8)	C(19)–O(5)–V ^a	122.32(14)	C(7)–C(8)–C(9)	119.9(2)
O(5)-V-O(2)	104.12(6)	V–O(5)–V ^a	106.61(7)	C(10)-C(9)-C(8)	120.1(2)
O(1)-V-O(3)	98.22(8)	C(11)–N(1)–N(2)	108.13(16)	C(9)-C(10)-C(5)	120.6(2)
O(5)-V-O(3)	89.99(6)	C(2)-N(2)-N(1)	115.71(16)	N(1)-C(11)-O(3)	122.24(18)
O(2)-V-O(3)	154.14(7)	C(2)–N(2)–V	127.58(14)	N(1)-C(11)-C(12)	119.57(18)
O(1)-V-N(2)	98.88(8)	N(1)-N(2)-V	116.29(12)	O(3)-C(11)-C(12)	118.10(18)
O(5)-V-N(2)	155.48(7)	N(2)-C(2)-C(3)	121.13(17)	C(13)-C(12)-C(17)	120.02(19)
O(2)-V-N(2)	83.91(7)	N(2)-C(2)-C(1)	120.63(19)	C(13)-C(12)-C(11)	118.90(19)
O(3)-V-N(2)	74.99(7)	C(3)-C(2)-C(1)	118.24(18)	C(17)-C(12)-C(11)	121.0(2)
O(1)-V-O(5) ^a	175.58(7)	C(4)-C(3)-C(2)	124.84(18)	C(14)-C(13)-C(12)	120.0(2)
O(5)-V-O(5) a	73.39(7)	O(2)-C(4)-C(3)	121.09(18)	O(4)-C(14)-C(13)	124.6(2)
O(2)-V-O(5) ^a	80.19(6)	O(2)-C(4)-C(5)	114.75(16)	O(4)-C(14)-C(15)	115.6(2)
O(3)-V-O(5) ^a	83.36(6)	C(3)-C(4)-C(5)	124.13(18)	C(13)-C(14)-C(15)	119.8(2)
N(2)-V-O(5) ^a	85.51(6)	C(6)-C(5)-C(10)	118.39(19)	C(16)-C(15)-C(14)	119.9(2)
C(4)–O(2)–V	133.70(12)	C(6)-C(5)-C(4)	121.75(18)	C(15)-C(16)-C(17)	121.4(2)
C(11)-O(3)-V	118.28(13)	C(10)-C(5)-C(4)	119.83(18)	C(16)-C(17)-C(12)	118.9(2)
C(14)-O(4)-C(18)	118.8(2)	C(7)-C(6)-C(5)	120.5(2)		

^a Symmetry transformations used to generate equivalent atoms: -x, -y+1, -z+1.

metal coordination spheres exert strong influence on the V...V separation, the hybridisation of the bridging oxygen, and hence the bridge angle about oxygen which is 106.61(7)°. Since the C(19)–O(5)–V angles exceed 120° , it transpires that the hybridisation of the oxygen is rather near sp². Dimeric vanadium chelates with a $\{VO(\mu_2-OR)_2VO\}^{4+}$ core may exist in five possible configurations classified according to the orientation of the vanadyl groups in respect to the plane defined by the vanadium centres and the bridging oxygen atoms [32]. The configurations are syn-orthogonal, anti-orthogonal, syn-coplanar, anti-coplanar, and twist. It has been suggested [33] that, when several structures differing very little in energy are possible, the centrosymmetric structure is preferred by crystal packing requirements. In dimeric vanadium chelates with a $\{VO(\mu_2 - \mu_2)\}$ $OR_{2}VO^{4+}$ core, the *anti*-structures are favorites. In the $[VO(m-CH_3Obhbzac)(\mu_2-OCH_3)]_2$ chelate, the atoms of the ligands are symmetrically disposed relative to the centre of the $\{VO(\mu_2-OR)_2VO\}^{4+}$ core and the disposition of the oxovanadium groups is anti-coplanar, a configuration sporadically encountered in dimeric oxovanadium compounds [34,35]. A clinographic projection of $[VO(m-CH_3Obhbzac)OCH_3]_2$ is shown in Fig. 2.



Fig. 2. A clinographic projection and labelling scheme of bis-[methoxo(4-phenyl-2,4-butanedione(3'-methoxybenzoyl)hydrazonato-(2-))-oxovanadium(V)]. The DIAMOND drawing shows the thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

4. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 134611 and 134612 for bis $[\mu_2$ -methoxo(4-phenyl-2,4-dione(3' - methoxybenzoyl)hydrazonato(2 -))oxovana-dium(V)] and [ethoxo(4-phenyl-2,4-dione(2'-nitrobenzoyl)hydrazonato(2-)oxovanadium(V)], respectively. Copies of this information 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).

References

- [1] A. Butler, C.J. Carrano, Coord. Chem. Rev. 109 (1991) 61.
- [2] D. Rehder, Angew. Chem., Int. Ed. 30 (1991) 148.
- [3] I. Cavaco, J.C. Pessoa, M. Duarte, R.D. Gillard, P. Matias, Chem. Commun. (1996) 1365.
- [4] M.F. Iskander, S. Saddek, Inorg. Chim. Acta 22 (1977) 141.
- [5] D.K. Rastogi, S.K. Sahni, V.B. Rana, S.K. Dua, J. Coord. Chem. 8 (1978) 97.
- [6] D.K. Rastogi, S.K. Sahni, V.B. Rana, K. Dua, S.K. Dua, J. Inorg. Nucl. Chem. 41 (1979) 21.
- [7] A.A. Diamantis, J.M. Frederiksen, M.A. Salam, M.R. Snow, E.R.T. Tiekink, Aust. J. Chem. 39 (1986) 1081.
- [8] K.C. Joshi, R. Bohra, B.S. Joshi, Inorg. Chem. 31 (1992) 598.
- [9] H.X. Liu, W. Wang, X. Wang, M.Y. Tan, J. Coord. Chem. 33 (1994) 347.
- [10] S.P. Rath, S. Mondal, A. Chakravorty, Inorg. Chim. Acta 263 (1997) 247.
- [11] L.J. Boucher, V.W. Day, Inorg. Chem. 16 (1977) 1360.
- [12] (a) R.C. Mehrota, R. Bohra, D.F. Gaur, Metal β-Diketonates and Allied Derivatives, Academic, London, 1978. (b) S. Di Bella, G. Lanza, A. Gulino, I. Fragala, Inorg. Chem. 35 (1996) 3885.
- [13] (a) D. Ogden, J. Selbin, J. Inorg. Nucl. Chem. 30 (1968) 1227.
 (b) H.J. Stoklosa, J.R. Wasson, J. Inorg. Nucl. Chem. 38 (1976)

677. (c) G.E. Mannix, A.P. Zipp, J. Inorg. Nucl. Chem. 41 (1979) 59.

- [14] C.J. Carrano, C.M. Nunn, R. Quan, J.A. Bonadies, V.L. Pecoraro, Inorg. Chem. 29 (1990) 944.
- [15] R.A. Rowe, M.M. Jones, Inorg. Synth. 5 (1957) 114.
- [16] J. Selbin, G. Maus, D.L. Johnson, J. Inorg. Nucl. Chem. 29 (1967) 1735.
- [17] K.F. Jahr, J. Fuchs, R. Oberhauser, Chem. Ber. 101 (1968) 482.
- [18] R.W. Layer, Chem. Rev. 63 (1963) 489.
- [19] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
- [20] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [21] A. Altomare, M.C. Burla, M. Cmalli, G. Cascarano, C. Giacovazzo, A. Gualiardi, A.G.G. Moliterni, G. Polidori, R. Spagna, SIR-97, A Package for Crystal Structure Solution by Direct Methods and Refinement, Roma, Italy, 1997.
- [22] (a) K. Bradenburg, DIAMOND (Version 2.1). Visual Crystal Structure Information System, Bonn University, 1998. (b) A. Dowltry, ATOMS (Version 4.1). A Computer Program for Displaying Molecular Structure, Shape Software, Kingsport, 1998.
- [23] J. Selbin, H.R. Manning, G. Cessac, J. Inorg. Nucl. Chem. 25 (1963) 1253.
- [24] E. Sinn, C.M. Harris, Coord. Chem. Rev. 4 (1969) 39.
- [25] N. Choudhary, D.L. Hughes, U. Kleinkes, L.F. Larkworthy, G.J. Leigh, M. Maiwald, C.J. Marmion, J.R. Sanders, G.W. Smith, C. Sudbrake, Polyhedron 16 (1997) 1517.
- [26] P.E. Figgins, D.H. Busch, J. Phys. Chem. 65 (1961) 2236.
- [27] S. Arrowsmith, M.F.A. Dove, N. Logan, A. Batsanov, Polyhedron 17 (1998) 421.
- [28] W. Wang, X. Wang, H.X. Liu, M.Y. Tan, J. Coord. Chem. 36 (1995) 49.
- [29] M. Velayutham, B. Varghese, S. Subramanian, Inorg. Chem. 37 (1998) 1336.
- [30] M. Root, J.D. Hoeschele, C.R. Cornman, J.W. Kampf, V.L. Pecoraro, Inorg. Chem. 32 (1993) 3855.
- [31] X. Wang, X.M. Zhang, H.X. Liu, Inorg. Chim. Acta 223 (1994) 193.
- [32] W. Plass, Angew. Chem., Int. Ed. Engl. 35 (1996) 627.
- [33] M.A. Porai-Koshits, Zh. Neorg. Khim. 13 (1968) 1233.
- [34] T. Carofiglio, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Polyhedron 15 (1996) 4435.
- [35] J. Salta, J. Zubieta, Inorg. Chim. Acta 257 (1997) 83.