New Non-oxo Vanadium-(IV) and -(V) Complexes†

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Sequential addition of 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy) followed by 3,5-di-*tert*-butylcatechol (H_2dtbc) to oxobis(pentane-2,4-dionato)vanadium(IV) yields [V(dtbc)$_2$L] (L = phen or bipy) which can be oxidised using Ag[SbF$_6$] to give [V(dtbc)$_2$L][SbF$_6$]. The new compounds have been characterised by microanalyses, IR, UV/VIS, ^{51}V NMR spectroscopy, magnetic susceptibility measurements and electrochemical studies. The X-ray structure of [V(dtbc)$_2$(bipy)] is reported and compared with those of [V(dtbc)$_2$(phen)] and [V(dtbc)$_2$(phen)][SbF$_6$].

It has been recognised that vanadium complexes have a significant role in a variety of biological systems such as marine organisms[1] and amavadin[2] whilst the vanadium containing protein derived from *Ascophyllum modosum* displays peroxidase activity.[3] Surprisingly, although the chemistry of oxovanadium-(IV) and -(V) complexes is well developed[4] far less work has been reported on non-oxo (so called 'bare') complexes. Although non-oxo vanadium-(IV) and -(V) complexes with all of the coordination sites occupied by oxygen donor ligands have been described there are only two examples of fully characterised vanadium(V) complexes,[5–8] [V(dtbc)$_3$]$^-$ and [V(N$_3$S$_2$)(dtbc)(phen)] (dtbc = 3,5-di-*tert*-butylcatecholate, phen = 1,10-phenanthroline). Here, we report on the synthesis and characterisation of complexes of the type [V(dtbc)$_2$L] and [V(dtbc)L]X (L = phen, 2,2′-bipyridine, X = SbF$_6^-$, BF$_4^-$), which are obtained *via* an unusual deoxygenation reaction of [VO(acac)$_2$] (acac = pentane-2,4-dionate). A preliminary communication[9] has compared the X-ray structures of [V(dtbc)$_2$(phen)] **1** and [V(dtbc)$_2$(phen)][SbF$_6$] **2** and highlighted substantial distortions from octahedral geometry for the vanadium(IV) complex. Here, the structure of the related vanadium(IV) complex [V(dtbc)$_2$(bipy)] **3** is also reported and compared with those of **1** and **2**.

Experimental

General.—All procedures were performed under argon using standard Schlenk line techniques or a glove-box. Diethyl ether, toluene and pentane were purified by refluxing over sodium and distillation under N$_2$. Dichloromethane and acetonitrile were refluxed over powdered calcium hydride and distilled under N$_2$. Chemicals were supplied by Aldrich. 3,5-Di-*tert*-butylcatechol was recrystallised twice from pentane, 2,2′-bipyridine was recrystallised from ethanol and phenanthroline was used as received. The complexes [VO(acac)$_2$] and [V(cat)(bzac)$_2$] (cat = catecholate, bzac = 1-phenylbutane-1,3-dionate) were prepared by the literature methods.[10,11] The purity of all starting materials was checked by elemental analyses and IR spectroscopy.

Elemental analyses were performed by the Imperial College Microanalytical Service or University College Microanalytical Service. Infrared spectra were measured as KBr discs or Nujol mulls using a PE 1720X spectrometer, UV/VIS spectra using septum sealed cuvettes and a Philips PU8740 spectrometer. Vanadium-51 NMR spectra were recorded using a Bruker WM250 spectrometer operating at 65.8 MHz with VOCl$_3$ as reference. Fast atom bombardment (FAB) mass spectra were obtained using a VG 2020 instrument and thiodiethanol matrix.

Electrochemical measurements were performed with a Metrohm E506 Polarecord-VA scanner and Houston 2000 recorder. Platinum wire and dropping mercury electrodes were employed as working electrodes for the cyclic voltammetry and polarographic studies respectively. Platinum wire was used as the auxiliary electrode and a calomel electrode in [NBu$_4$][BF$_4$]-saturated CH$_2$Cl$_2$ or MeCN was used as the reference; 0.1 mol dm^{-3} [NBu$_4$][BF$_4$] was used as the supporting electrolyte with the solutions being 10^{-3}–10^{-4} mol dm^{-3} in complex. Values of the reduction potentials ($E_{\frac{1}{2}}$) were obtained from intercepts of $\log[(i_d - i)/i]$ *versus* E plots. The number of electrons involved in the reversible electrode processes were estimated from the slopes of such plots according to the Heyrovsky–Ilkovic equation[8] $\{E = E_{\frac{1}{2}} + (RT/nF)\ln[(i_d - i)/i]\}$. All potentials are reported relative to the normal hydrogen electrode (NHE)[12] and were referenced using ferrocene (+0.400 *versus* NHE).[13]

Magnetic moments were measured at room temperature by the Faraday method using a Cahn–Ventron RM-2 balance [HgCo(CN)$_4$ as standard].

Preparation of the Complexes.—[V(dtbc)$_2$(phen)]·CH$_2$Cl$_2$ **1**. Phenanthroline (1.35 g, 7.5 mmol) in CH$_2$Cl$_2$ (8 cm^3) was added to a suspension of [VO(acac)$_2$] (2.00 g, 7.5 mmol) in CH$_2$Cl$_2$ (20 cm^3). The solution cleared and its colour changed from blue to green. 3,5-Di-*tert*-butylcatechol (H_2dtbc) (3.35 g, 15 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added to the stirred solution whereupon a dark black precipitate was formed and the solution became deep blue. After stirring for 30 min the solution was filtered and the precipitate washed with CH$_2$Cl$_2$ (2 × 10 cm^3) and dried *in vacuo*. Yield 5.39 g, 95%. Mass spectrum: *m*/*z* (relative intensity %) [identity], 673 (19) [*M*H$_2$], 672 (59) [*M*H], 671 (100) [*M*], 467 (17) [VO(dtbc)(phen)], 247 (65) [VO(phen)], 181 (75) [Hphen].

[V(dtbc)$_2$(phen)][SbF$_6$]·CH$_2$Cl$_2$ **2**. Silver hexafluoroantimonate (1.023 g, 3 mmol) was added to a stirred suspension of **1** (2.0 g, 2.6 mmol) in CH$_2$Cl$_2$ (20 cm^3). The solution immediately cleared, became sky-blue and after a few minutes silver was precipitated. After stirring for 2 h the solution was filtered. Pentane (80 cm^3) was added dropwise to the filtrate and the resulting precipitate was filtered off, washed with pentane until

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

the washings were colourless and dried *in vacuo*. Yield 2.47 g, 94%.

[V(dtbc)$_2$(bipy)] **3** *and* [V(dtbc)$_2$(bipy)][SbF$_6$] **4**. These complexes were prepared in a similar way to **1** and **2** and were obtained in 75 and 80% yield respectively. Mass spectrum: **3** 648 (8) [*M*], 444 (23) [VO(dtbc)(bipy)H$_2$], 443 (65) [VO(dtbc)(bipy)], 223 (23) [VO(bipy)], 157 (25) [Hbipy].

[V(dtbc)$_2$(phen)][BF$_4$] **5** *and* [V(dtbc)$_2$(bipy)][BF$_4$] **6**. These complexes were prepared in a similar fashion to **2** and **4** using Ag[BF$_4$] and were obtained in 80 and 75% yield respectively.

Complexes **1**–**5** were usually obtained with solvated CH$_2$Cl$_2$ and although it was possible to remove some of the solvate molecules by extending drying *in vacuo* we were unable to obtain the complexes free of dichloromethane.

Crystals of [V(dtbc)$_2$(bipy)]·C$_6$H$_5$Me suitable for X-ray analysis were obtained by slow diffusion of pentane into a concentrated toluene solution of the complex.

Crystallography.—Crystal data. **3** $C_{38}H_{48}N_2O_4V{\cdot}C_7H_8$, $M = 739.9$, monoclinic, space group $P2_1/a$, $a = 15.370(3)$, $b = 16.810(3)$, $c = 17.201(3)$ Å, $\beta = 109.37(2)°$, $U = 4193$ Å^3, $Z = 4$, $D_c = 1.17$ g cm^{-3}, μ(Cu-Kα) = 23 cm^{-1}, $\bar{\lambda} = 1.541\,78$ Å, $F(000) = 1580$.

Data collection and processing. Nicolet R3m diffractometer, ω-scan method, ($2\theta \leqslant 116°$), graphite monochromated Cu-Kα radiation; 5655 independent measured reflections, 3803 observed [$|F_o| > 3\sigma(|F_o|)$], corrected for Lorentz and polarisation factors; no absorption correction.

Structure analysis and refinement. The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. A ΔF map revealed the presence of a toluene molecule and disorder in two of the *tert*-butyl groups. Both of these were refined with two partial site occupancy orientations. The occupancies were 0.75 and 0.25 for the methyl groups on C(21) and 0.70 and 0.30 for the groups on C(35). The major-occupancy carbon atoms were refined anisotropically and the minor-occupancy atoms isotropically. There was high thermal anisotropy in the toluene molecule but this could not be resolved into discrete alternative orientations. The leading proton on the methyl group of the toluene was located from a ΔF map. The positions of the remaining hydrogen atoms were idealised (C–H 0.96 Å), assigned isotropic thermal parameters $U(\mathrm{H}) = 1.2U_{eq}(\mathrm{C})$ and allowed to ride on their parent carbons. The toluene molecule and the methyl groups were refined as rigid bodies. The low-occupancy hydrogen atoms of the disordered *tert*-butyl groups were not included. Refinement was by full-matrix least squares to $R = 0.076$ ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$), $R' = 0.076$ [$\Sigma w^{\frac{1}{2}}\Delta F/\Sigma w^{\frac{1}{2}}F_o$, $w^{-1} = \sigma^2(F) + 0.001\,00F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.48 and -0.34 e Å^{-3} respectively and the mean and maximum shifts/error in the final refinement cycle were 0.030 and 0.726 respectively. Computations were carried out using the SHELXTL PC program system.[14]

Results and Discussion

The vanadium(IV) complexes **1** and **3** were prepared by a modification of the method reported by Galeffi and Postel[15] according to equation (1) with sequential addition of L (phen or bipy) followed by H$_2$dtbc.

$$[\mathrm{VO(acac)_2}] + \mathrm{L} + 2\mathrm{H_2dtbc} \longrightarrow [\mathrm{V(dtbc)_2L}] + \mathrm{H_2O} + 2\mathrm{Hacac} \quad (1)$$

In particular we found that the reaction proceeds smoothly in a much lower volume (*ca.* 10%) of solvent (CH$_2$Cl$_2$) since the addition of phen or bipy to the suspension of [VO(acac)$_2$] immediately clears the solution, furthermore the total reaction time was reduced since the reaction with H$_2$dtbc is immediate. An especially interesting feature of the reaction is the deoxygenation of the oxovanadium(IV) by H$_2$dtbc. Previously, it has been reported[5] that if H$_2$dtbc is treated with [VO(acac)$_2$] in a molar ratio of 3.55:1 in the presence of excess NEt$_3$ the product is [NHEt$_3$][VO(dtbc)$_2$]. It seems likely that the initial product from the reaction in equation (1) is seven-co-ordinate [VO(acac)$_2$(phen)], which as a consequence of its high co-ordination number has a weakened V=O bond. Other workers[16] have reported the deoxygenation of V=O in the formation of the eight-co-ordinate complex bis(*N*-hydroxyiminodiacetato)vanadium(IV).

Oxidation of compounds **1** and **3** is readily accomplished using Ag[SbF$_6$] [equation (2)] with the soluble product being

$$[\mathrm{V(dtbc)_2L}] + \mathrm{Ag[SbF_6]} \longrightarrow [\mathrm{V(dtbc)_2L}][\mathrm{SbF_6}] + \mathrm{Ag} \quad (2)$$

readily separated from the Ag[SbF$_6$] and silver. Attempts to form the vanadium(III) complexes using cobaltocene and NaBH$_4$ were unsuccessful.

Microanalytical data for the new complexes are given in Table 1. In general the IR data are not especially informative; in common with previous reports[17,18] upon metal catecholates we observe intense bands at 1450–1480 cm^{-1} (ring stretching) and 1250–1290 cm^{-1} ν(CO). In the SbF$_6^-$ complexes strong bands due to this anion are observed at 656 and 290 cm^{-1}.

The results of DC-cyclic voltammetry (CV) and polarographic studies in CH$_2$Cl$_2$ and MeCN upon **1** and **3** are given in Table 2 and illustrated for **1** in CH$_2$Cl$_2$ in Fig. 1. The polarographic studies in acetonitrile reveal a reversible one-

Table 1 Microanalytical data * for the complexes

Complex	C	H	N
1 [V(dtbc)$_2$(phen)]·CH$_2$Cl$_2$	65.1 (65.1)	6.8 (6.7)	3.7 (3.7)
2 [V(dtbc)$_2$(phen)][SbF$_6$]·CH$_2$Cl$_2$	49.9 (49.6)	5.2 (5.1)	2.9 (2.8)
3 [V(dtbc)$_2$(bipy)]·CH$_2$Cl$_2$	63.8 (63.9)	6.9 (6.9)	3.8 (3.8)
4 [V(dtbc)$_2$(bipy)][SbF$_6$]·CH$_2$Cl$_2$	48.8 (48.4)	5.3 (5.2)	2.8 (2.9)
5 [V(dtbc)$_2$(phen)][BF$_4$]·CH$_2$Cl$_2$	58.6 (58.4)	5.8 (5.7)	3.2 (3.3)
6 [V(dtbc)$_2$(bipy)][BF$_4$]	62.3 (62.1)	6.7 (6.6)	3.7 (3.8)

* Required values are given in parentheses.

Table 2 Electrochemical data for **1** and **3** from CV and polarographic studies[a]

Complex	Solvent	E_{pc}/V	E_{pa}/V	i_{pc}/i_{pa}	ΔE_p/mV[b]	$E_{\frac{1}{2}}$/V[c]
1	CH$_2$Cl$_2$	−0.96	−0.84	1.00	120	−0.90 (−0.89)[d]
		0.34	0.46	1.00	120	0.40 (0.42)
	MeCN	−0.77	−0.71	1.00	60	−0.74 (−0.79)
		0.49	0.55	1.00	60	0.52
3	CH$_2$Cl$_2$	−0.92	−0.80	1.00	120	−0.86 (−0.88)
		0.41	0.53	1.00	120	0.47 (0.48)
	MeCN	−0.76	−0.70	1.01	60	−0.73 (−0.71)
		0.51	0.58	1.02	70	0.545

[a] All potentials are *vs.* NHE. [b] $\Delta E_p = E_{pc} - E_{pa}$ at a scan rate of 100 mV s^{-1}. [c] $E_{\frac{1}{2}}$ calculated using the formula 0.5 ($E_{pc} + E_{pa}$) from cyclic voltammetry. [d] Values of the reduction potentials (in parentheses) from the intercepts of plots of $\ln[(i_d - i)/i]$ *vs.* potential.

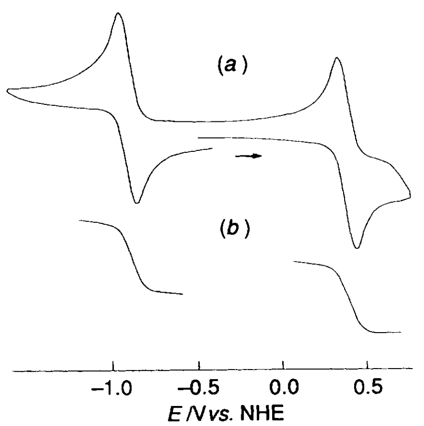

Fig. 1 (*a*) DC cyclic voltammogram for the oxidation and reduction of compound **1** (10^{-3} mol dm^{-3}) in CH_2Cl_2 with $[NBu_4][BF_4]$ (0.1 mol dm^{-3}) at a platinum electrode with a scan rate of 100 mV s^{-1}; (*b*) DC polarogram of the same solution as in (*a*) at a dropping mercury electrode

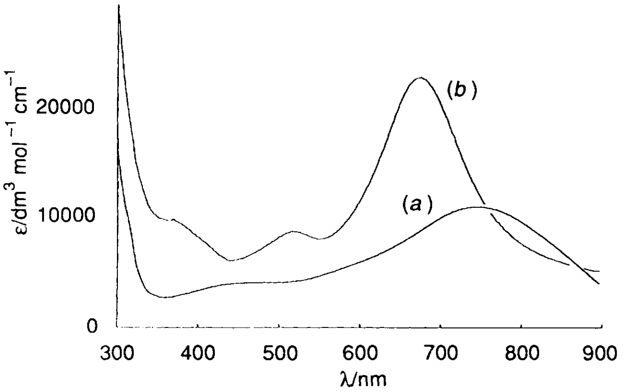

Fig. 2 Optical spectra of (*a*) $[V(dtbc)(phen)]\cdot CH_2Cl_2$ and (*b*) $[V(dtbc)_2(phen)][SbF_6]$ in dichloromethane

Table 3 UV/VIS spectral data for the complexes (in CH_2Cl_2)

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
1	750 (11 660), 487 (sh) (4735), 277 (30 470), 221 (50 000)
3	735 (11 280), 491 (sh) (4480), 313 (15 000), 277 (17 600), 222 (44 100)
2	675 (22 600), 516 (4050), 402 (sh) (4500), 272 (41 000), 224 (54 500)
4	676 (22 400), 510 (sh) (3500), 404 (sh) (3700), 294 (23 100), 240 (sh) (25 400), 220 (44 600)

electron redox process at −0.79 and −0.71 V for **1** and **3** respectively whereas in CH_2Cl_2 two reversible one-electron processes at −0.89, 0.42 and −0.88, 0.48 V (*vs.* NHE) are observed. Cyclic voltammetric studies in both solvents show two redox couples for each complex. The peak separation in acetonitrile (ΔE_p) is close to that anticipated for a Nernstian process (59 mV) whilst in dichloromethane the value is increased to 120 mV.* Plots of peak current *versus* scan rate are linear and the ratios of the cathodic and anodic peak currents are unity indicating that the electron transfer is reversible with negligible mass transfer. A blank CV run of H_2dtbc in the potential range −1.6 to 1.3 V (*vs.* NHE) reveals one peak at *ca.* +1.0 V due to oxidation of the ligand. Since phen and bipy are both electrochemically inert over the range studied here we conclude that both of the redox processes we observe are metal based [illustrated for the phen complex in MeCN in equations (3) and (4)].

$$[V(dtbc)_2(phen)]^+ + e^- \rightleftharpoons [V(dtbc)_2(phen)] \quad E_{\frac{1}{2}} = 0.52\ V \qquad (3)$$

$$[V(dtbc)_2(phen)] + e^- \rightleftharpoons [V(dtbc)_2(phen)]^- \quad E_{\frac{1}{2}} = -0.79\ V \qquad (4)$$

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* Ferrocene was used as a secondary internal reference ($E_{\frac{1}{2}}$ +0.60 V *vs.* SCE, peak separation 110 mV) as described previously.[8]

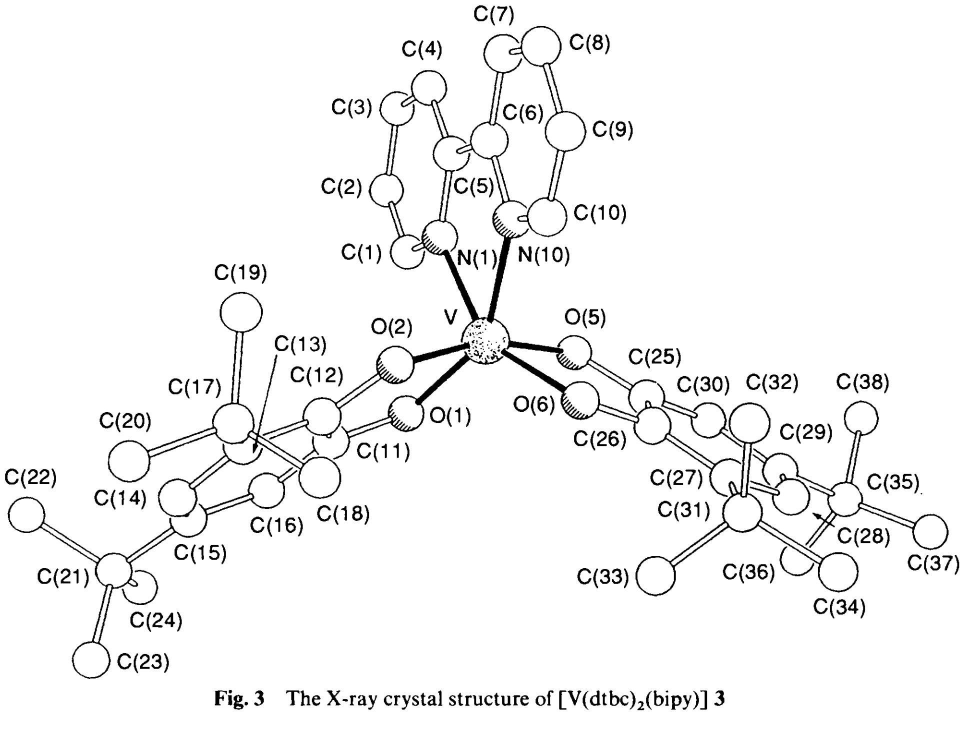

Fig. 3 The X-ray crystal structure of $[V(dtbc)_2(bipy)]$ **3**

Table 4 Atomic coordinates (× 10⁴) with estimated standard deviations (e.s.d.s) for compound **3**

Atom	*x*	*y*	*z*
V	−2085.7(7)	−1365.9(6)	−609.5(6)
N(1)	−877(3)	−1138(3)	−922(3)
C(1)	−312(5)	−1716(4)	−1009(4)
C(2)	490(5)	−1565(4)	−1157(5)
C(3)	738(5)	−790(5)	−1222(4)
C(4)	164(5)	−192(4)	−1141(4)
C(5)	−635(4)	−380(4)	−987(3)
C(6)	−1315(4)	211(3)	−903(3)
C(7)	−1239(5)	1017(4)	−996(4)
C(8)	−1931(6)	1502(4)	−922(5)
C(9)	−2660(5)	1174(4)	−743(5)
C(10)	−2698(5)	376(4)	−666(4)
N(10)	−2030(3)	−108(3)	−723(3)
O(1)	−2083(3)	−2408(2)	−1057(2)
O(2)	−3130(2)	−1283(2)	−1569(2)
C(11)	−2734(4)	−2545(3)	−1790(3)
C(12)	−3348(4)	−1913(3)	−2079(3)
C(13)	−4091(4)	−1970(3)	−2812(3)
C(14)	−4164(4)	−2686(3)	−3222(4)
C(15)	−3559(4)	−3322(3)	−2965(4)
C(16)	−2836(4)	−3250(3)	−2227(3)
C(17)	−4801(4)	−1298(4)	−3086(4)
C(18)	−5289(5)	−1209(5)	−2450(5)
C(19)	−4330(5)	−519(4)	−3161(5)
C(20)	−5533(6)	−1479(4)	−3921(5)
C(21)	−3708(5)	−4072(4)	−3498(4)
C(22)	−3574(9)	−3862(6)	−4332(6)
C(23)	−4674(7)	−4401(6)	−3664(8)
C(24)	−3004(7)	−4731(5)	−3101(6)
C(22′)	−2856(16)	−4378(24)	−3637(25)
C(23′)	−4543(17)	−4158(21)	−4254(15)
C(24′)	−3842(30)	−4762(16)	−2985(21)
O(5)	−1232(3)	−1684(2)	435(2)
O(6)	−2844(3)	−1199(2)	69(2)
C(25)	−1572(4)	−1704(3)	1062(4)
C(26)	−2490(4)	−1422(3)	847(3)
C(27)	−2934(4)	−1416(3)	1436(4)
C(28)	−2438(5)	−1706(3)	2210(4)
C(29)	−1546(5)	−2016(4)	2432(4)
C(30)	−1114(5)	−1994(3)	1837(4)
C(31)	−3931(4)	−1091(3)	1220(4)
C(32)	−3951(5)	−212(4)	973(4)
C(33)	−4593(5)	−1565(4)	508(5)
C(34)	−4286(5)	−1133(4)	1957(4)
C(35)	−1079(7)	−2373(4)	3292(4)
C(36)	−1029(10)	−3259(5)	3160(6)
C(37)	−1520(11)	−2150(9)	3908(7)
C(38)	−25(9)	−2048(8)	3601(7)
C(36′)	−1709(20)	−3024(17)	3407(20)
C(37′)	−1015(20)	−1832(15)	4000(14)
C(38′)	−135(12)	−2719(20)	3471(19)
C(40)	−2133(4)	−273(5)	−3810(4)
C(41)	−2683	−238	−4637
C(42)	−3045	−935	−5062
C(43)	−2857	−1667	−4658
C(44)	−2307	−1702	−3831
C(45)	−1945	−1005	−3407
C(46)	−1770	458	−3381

Compounds **1** and **3** have an N_2O_4 co-ordination sphere and it is of interest to compare this with a recently reported[19] N_3O_3 co-ordinated system, [1,4,7-tris(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononanato(3−)]vanadium(IV) **7** which has similar properties to **1** and **3** (for **7** $V^V \rightleftharpoons V^{IV}$ $E_{\frac{1}{2}}$ +0.78, $V^{IV} \rightleftharpoons V^{III}$ −0.10, $V^{III} \rightleftharpoons V^{II}$ −2.01 V, *vs.* NHE). In both cases the electrochemical studies indicate that the thermodynamically most stable species is vanadium(IV) but the N_2O_4 system is quite stable to reduction and moderately stable to oxidation whereas the N_3O_3 system is readily reduced to V^{III} but not readily oxidised. A further reduction to V^{II} seen for the N_3O_3 systems is not observed for the N_2O_4 complexes described here. Although there are a number of factors involved, the difference in properties of the two co-ordination shells presumably reflects (*i*) the difference in overall ligand charge (−4 for **1** *versus* −3 for **7**) and (*ii*) the ability of the softer nitrogen atoms to stabilise the lower (softer) oxidation states in the N_3O_3 case.

The electronic absorption spectra are given in Table 3 with the spectra for **1** and **2** being displayed in Fig. 2. The very intense low-energy transition is assigned as ligand-to-metal charge-transfer,[5,11,17,20,21] which shifts to lower energy upon increasing the formal oxidation number. This is in marked contrast to the observations of Wieghardt and co-workers.[19] The molar absorptions observed here are remarkably high, indeed we know of only one example in the literature with higher absorption coefficients.[19] It is particularly noticeable that the (symmetric) tris(*tert*-butylcatecholato) complexes previously reported[5,6] have substantially lower absorption coefficients compared to the complexes reported here.

Compounds **1** and **3** have magnetic moments of 1.76 and 1.78 μ_B respectively as expected for a d^1 system whereas the oxidised analogues are diamagnetic. The ^{51}V NMR spectra of **5** and **6** consist of broad ($\nu_{\frac{1}{2}}$ *ca.* 1000 Hz) lines at δ −202 and −235 respectively; we have not been able to observe signals for the SbF_6^- salts **2** and **4**.

The X-ray crystal structure of **3** is illustrated in Fig. 3; Tables 4 and 5 give the fractional atomic coordinates and a comparison of selected bond lengths and angles for **1**–**3**. In common with **1**

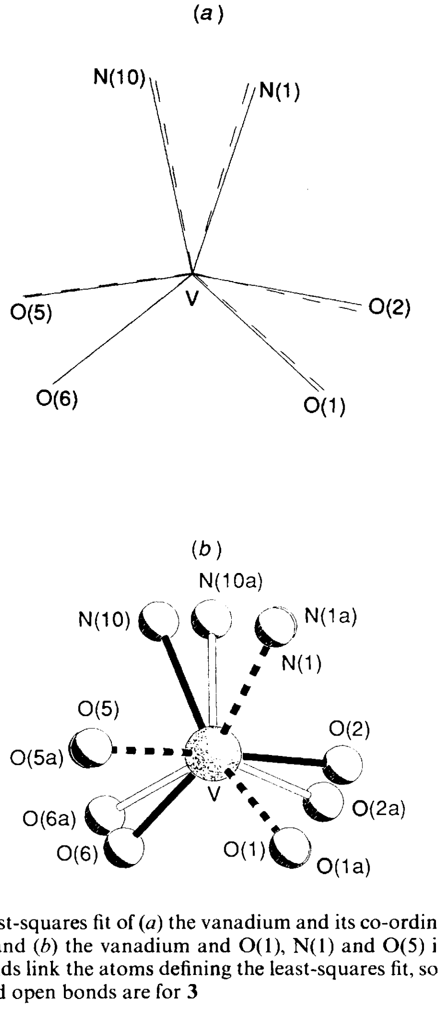

Fig. 4 Least-squares fit of (*a*) the vanadium and its co-ordination shell in **1** and **3** and (*b*) the vanadium and O(1), N(1) and O(5) in **2** and **3**. Dashed bonds link the atoms defining the least-squares fit, solids bonds are for **2** and open bonds are for **3**

Table 5 Comparison of selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compounds **1**–**3**

	1*	**2***	**3**
V–N(1)	2.122(12)	2.116(9)	2.134(6)
V–N(10)	2.171(11)	2.115(8)	2.128(4)
V–O(1)	1.926(9)	1.903(6)	1.914(4)
V–O(2)	1.885(11)	1.892(7)	1.888(3)
V–O(5)	1.897(11)	1.896(6)	1.916(4)
V–O(6)	1.918(9)	1.875(7)	1.925(5)
mean C–O	1.34	1.32	1.34
N(1)–V–N(10)	74.6(5)	78.1(3)	74.6(2)
O(1)–V–O(2)	81.4(4)	80.2(3)	80.2(2)
O(5)–V–O(6)	80.3(4)	81.0(3)	80.6(2)
N(1)–V–O(1)	85.3(4)	88.7(3)	86.8(2)
N(1)–V–O(2)	104.3(4)	91.1(3)	109.0(2)
N(10)–V–O(1)	151.8(4)	165.1(3)	150.1(2)
N(10)–V–O(2)	84.6(5)	92.9(3)	84.0(2)
N(1)–V–O(5)	85.8(5)	88.0(3)	84.5(2)
N(10)–V–O(5)	108.3(5)	91.7(3)	109.1(2)
O(1)–V–O(5)	89.3(4)	94.8(3)	91.7(2)
O(2)–V–O(5)	165.6(4)	175.0(3)	163.7(2)
N(1)–V–O(6)	153.0(5)	165.7(3)	151.7(2)
N(10)–V–O(6)	87.9(4)	92.9(3)	87.8(2)
O(1)–V–O(6)	117.4(4)	101.3(3)	117.4(2)
O(2)–V–O(6)	94.1(5)	100.6(3)	90.5(2)

* From ref. 9.

and **2**, **3** crystallises in a centrosymmetric space group with both Δ and Λ forms present. Also, as with **1** and **2** the most sterically demanding isomer, *i.e.*, that with the two 3-*tert*-butyl groups *syn* is observed. The geometry of the vanadium co-ordination sphere is virtually identical to that of **1** with maximum deviations of the least-squares fit of 0.08 Å for N(1) and O(2) [Fig. 4(*a*)]. This observation lends additional weight to the preliminary observations about the principal differences between the structures of the V^{IV} and V^{V} centres in **1** and **2**.[9] The most striking difference in the co-ordination geometry on going from V^{V} to V^{IV} in these complexes (despite differences in the neutral bidentate N-donor ligand, phen or bipy) is a transformation from slightly distorted octahedral geometry towards trigonal prismatic geometry upon reduction. Fig. 4(*b*) compares the co-ordination geometry of **2** and **3** as a least-squares fit, based upon the vanadium together with O(1), N(1) and O(5) which represent one face of the octahedron. Whereas the maximum deviation of the least-squares fit for these four atoms is 0.05 Å the remaining three atoms deviate by 0.68, 0.57 and 0.53 Å for N(1), O(2) and O(6) respectively. This is equivalent to a rotation of 22° about one of the 'S_6' axes of the ideal octahedron by the lower octahedral face with respect to the upper face. The structure of **3** supports our earlier conclusion that the oxidation state of the vanadium has a major influence on the co-ordination bond angles but not the bond lengths in these type of complexes. We conclude that an analysis of the co-ordination geometry in tris-chelate vanadium complexes may be used as a diagnostic tool to distinguish V^{V} from V^{IV}.

Acknowledgements

We are grateful to the SERC for equipment, to the Wolfson Foundation for Support and to Ciba Geigy for an ACE award.

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Received 28*th November* 1991; *Paper* 1/06034A