Phenoxo and Diphenoxo Complexes of Titanium(III) and Vanadium(III): Synthesis and *X*-Ray Structure†

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Reaction of $[TiCl_3(thf)_3]$ and $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) with 2,6-$Bu^t_2C_3H_3ONa$ and 2,6-$Me_2C_6H_3ONa$ respectively, led to the monomeric five-co-ordinate complexes $[TiCl_2(2,6\text{-}Bu^t_2C_6H_3O)(thf)_2]$, (**1**), and $[VCl_2(2,6\text{-}Me_2C_6H_3O)(thf)_2]$, (**2**). Both metal atoms have a trigonal bipyramidal co-ordination, the equatorial plane being defined by the two chloride and the phenoxo ligands. The axial positions are filled by two thf molecules. Phenoxo parameters are: Ti–O 1.807(8) and V–O 1.803(5) Å; Ti–O–C 174.2(9) and V–O–C 135.9(5)°. Reaction of the sodium salt of benzene-1,2-diol (H_2cat) with $[VCl_3(thf)_3]$ led to the isolation of a binuclear complex $[V_2(\mu\text{-}cat)_2Cl_2(thf)_4]$, (**3**), while the reaction with the sodium salt of bis(2-hydroxy-5-methyl-3-t-butylphenyl)methane (H_2bhm) gave the mononuclear complex $[V(bhm)Cl(thf)_2]$ (**4**). Complex (**3**) has a planar $V_2(\mu\text{-}cat)_2Cl_2$ skeleton with molecules of thf above and below the plane, and vanadium(III) achieves six-co-ordination by sharing the oxygens of the catecholato dianion. Complex (**4**) has a monomeric structure with the diphenolato anion (bhm) forming an eight-membered ring and vanadium(III) having a pseudo-trigonal-bipyramidal co-ordination. Compounds (**1**)—(**4**) (all monoclinic) were characterized by single-crystal *X*-ray analysis: (**1**), space group $P2_1/c$, a = 10.483(1), b = 10.771(1), c = 24.847(2) Å, β = 95.61(1)°, Z = 4, R 0.064 for 1 051 observed reflections; (**2**), space group $P2_1/n$, a = 7.329(1), b = 13.195(1), c = 19.687(2) Å, β = 94.58(1)°, Z = 4, R 0.057 for 1 226 observed reflections; (**3**), space group $P2_1/n$, a = 17.743(2), b = 9.238(1), c = 9.522(1) Å, β = 97.35(1)°, Z = 2, R 0.043 (R' 0.047) for 1 264 observed reflections; (**4**), space group $P2_1/c$, a = 9.327(1), b = 13.814(2), c = 24.577(2) Å, β = 93.54(1)°, Z = 4, R 0.059 (R' 0.065) for 2 390 observed reflections.

The phenoxo functionality seems to be a special ancillary ligand in titanium[1–3] and vanadium[4,5] precursors of active species in dinitrogen reduction processes. In addition, the use of phenoxides as supporting ligands for organometallic functionalities in early transition-metal organic chemistry has recently been reported.[6,7] In this context, we report the synthesis and the structural characterization of monomeric and dimeric complexes of titanium(III) and vanadium(III) containing a reducible and functionalizable metal centre, which shows a potentially high co-ordinative unsaturation.

Experimental

All syntheses were carried out under an atmosphere of purified nitrogen. Solvents were purified and dried by standard methods. Infrared spectra were recorded with a Perkin-Elmer 983 spectrophotometer and magnetic measurements made using a Faraday balance. The compounds $[VCl_3(thf)_3]$ and $[TiCl_3(thf)_3]$ (thf = tetrahydrofuran) were prepared by a published procedure.[8] The sodium salts of phenols were prepared by treating them with NaH in thf. The compound bis(2-hydroxy-5-methyl-3-t-butylphenyl)methane (H_2bhm) was supplied by the Ciba-Geigy Company (Basel).

Syntheses.—$[TiCl_2(2,6\text{-}Bu^t_2C_6H_3O)(thf)_2]$, (**1**). The sodium salt of 2,6-$Bu^t_2C_6H_3OH$ (8.02 g, 35.2 mmol) was added at room temperature to a stirred thf (100 cm^3) suspension of $[TiCl_3(thf)_3]$ (13.06 g, 35.3 mmol). A very fast reaction produced an emerald-green solution with some undissolved solid. The suspension was refluxed overnight, then the solvent was evaporated to dryness. The solid residue was dissolved in toluene (70 cm^3) and NaCl removed by filtration. By addition of n-hexane (100 cm^3) a green crystalline solid formed and was dried *in vacuo* (10.3 g, yield 62.3%) (Found: C, 57.00; H, 8.10; Cl, 14.90. $C_{22}H_{37}Cl_2O_3Ti$ requires C, 56.45; H, 7.90; Cl, 15.15%), $\mu_{eff.}$ = 1.79 at 295.4 K. The *X*-ray analysis was performed on the solvated form $[TiCl_2(2,6\text{-}Bu^t_2C_6H_3O)(thf)_2]\cdot0.5C_7H_8$.

$[VCl_2(2,6\text{-}Me_2C_6H_3O)(thf)_2]$, (**2**). Sodium hydride (1.02 g, 42.5 mmol) was added to a solution of 2,6-$Me_2C_6H_3OH$ (5.6 g, 45.9 mmol) in thf (100 cm^3). The suspension was stirred until complete dissolution of the solid, then $[VCl_3(thf)_3]$ (15.80 g, 42.3 mmol) was added. The resulting red suspension was stirred overnight. The solvent was evaporated to dryness and the residue collected with n-hexane (300 cm^3). The suspension was filtered when hot and the red solution so obtained cooled at room temperature, then to −30 °C, to give red crystals of the complex (11.5 g, 70.5%) (Found: C, 48.95; H, 6.75; Cl, 18.10. $C_{16}H_{25}Cl_2O_3V$ requires C, 49.65; H, 6.45; Cl, 18.30%), $\mu_{eff.}$ = 2.87 at 295 K.

$[V_2(\mu\text{-}cat)_2Cl_2(thf)_4]$, (**3**). The sodium salt of benzene-1,2-diol (H_2cat) (50.2 mmol) was added as a solid to a thf (250 cm^3) suspension of $[VCl_3(thf)_3]$ (18.8 g, 50.3 mmol). The addition must be slow since the reaction is highly exothermic. The resulting red-brown suspension was filtered when hot in order to remove NaCl. A significant amount of the solid is removed with NaCl. The resulting solution gave on cooling at room

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Experimental data for the *X*-ray diffraction study of complexes (**1**)—(**4**)[a]

Complex	(**1**)	(**2**)	(**3**)	(**4**)
Formula	$C_{22}H_{37}Cl_2O_3Ti{\cdot}0.5C_7H_8$	$C_{16}H_{25}Cl_2O_3V$	$C_{28}H_{40}Cl_2O_8V_2$	$C_{31}H_{46}ClO_4V$
M	514.4	387.2	677.4	569.1
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Cell parameters[b]				
a/Å	10.483(1)	7.329(1)	17.743(2)	9.327(1)
b/Å	10.771(1)	13.195(1)	9.238(1)	13.814(2)
c/Å	24.847(2)	19.687(2)	9.522(1)	24.577(2)
β/°	95.61(1)	94.58(1)	97.35(1)	93.54(1)
U/Å^3	2 792.1(4)	1 897.8(4)	1 547.9(3)	3 160.5(6)
Z	4	4	2	4
D_c/g cm^{-3}	1.224	1.355	1.453	1.196
F(000)	1 096	808	704	1 216
Crystal size/mm	0.16 × 0.27 × 0.50	0.18 × 0.37 × 0.65	0.11 × 0.23 × 0.25	0.32 × 0.45 × 0.52
μ/cm^{-1}	5.17	7.97	8.02	4.18
2θ range/°	6—45	6—46	6—46	6—47
Unique total data	3 542	2 657	2 151	4 670
Criterion for 'observed'	$I > 1.5\sigma(I)$	$I > 1.5\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Unique obs. data	1 051	1 226	1 264	2 390
R[c]	0.064	0.057	0.043	0.059
R'[d]	—		0.047	0.065

[a] Details common to the four determinations: crystal system, monoclinic; diffractometer PW 1100; scan type, ω—2θ; radiation, graphite-monochromatized Mo-K_α (λ = 0.710 69Å). [b] Unit-cell parameters were obtained by least-squares analysis of the setting angles of 25—30 carefully centred reflections chosen from diverse regions of reciprocal space. [c] $\Sigma|\Delta F|/\Sigma|F_o|$. [d] $\Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F_o|$.

temperature a deep red crystalline solid (yield 60%). In order to increase the yield we adopted an extraction with thf for removing all the product from NaCl (Found: C, 48.90; H, 6.05; Cl, 10.65. $C_{28}H_{40}Cl_2O_8V_2$ requires C, 49.65; H, 5.90; Cl, 10.45%), $\mu_{eff.}$ = 2.86 at 293 K.

[V(bhm)Cl(thf)$_2$], (**4**). A thf (250 cm^3) suspension of H_2bhm (27.5 g, 80.8 mmol) was treated with NaH (3.86 g, 160.8 mmol) and stirred until the reaction was complete. The resulting solution was freed from a small amount of solid by filtration. Solid [VCl$_3$(thf)$_3$] (30.2 g, 80.8 mmol) was added on stirring. A violet suspension was obtained from which NaCl was removed by filtration. The resulting solution was evaporated to dryness and the solid residue treated with hot n-hexane in which it partially dissolved. The n-hexane solution gave on cooling at 0 °C a red-violet crystalline solid (yield 45%) (Found: C, 65.50; H, 8.25; Cl, 6.10. $C_{31}H_{46}ClO_4V$ requires C, 65.40; H, 8.10; Cl, 6.25%), $\mu_{eff.}$ = 2.80 at 293 K.

X-Ray Structure Determinations.—The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Data were collected at room temperature on a single-crystal four-circle diffractometer. Crystal data and details of the parameters associated with data collection are given in Table 1. The reduced cells quoted were obtained with the use of TRACER.[9] For intensities and background individual reflection profiles were analyzed for complexes (**1**) and (**2**),[10] while the 'three-point' technique was used for (**3**) and (**4**). The structure amplitudes were obtained after the usual Lorentz and polarization corrections[11] and the absolute scale was established by the Wilson method.[12] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected in all cases. The function minimized during the least-squares refinement was $\Sigma w|\Delta F|^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$ for complexes (**3**) and (**4**). At the end of the refinement the values for *k* and *g* were 0.9403 and 0.000 907, 1.3088 and 0.001 533 for (**3**) and (**4**) respectively. For complexes (**1**) and (**2**) unit weights were applied leading to better agreement analyses and indices. Anomalous scattering corrections were included in all structure-factor calculations.[13a] Neutral atom scattering factors were taken from ref. 13*b* for non-hydrogen atoms and from ref. 14 for hydrogen atoms. Among the low-angle reflections no correction for secondary extinction was deemed necessary. The structures were solved by the heavy-atom method (Patterson and Fourier techniques) and refined by full-matrix least squares. The hydrogen atoms, either located from a difference map or put in geometrically calculated positions, were introduced in the final stage of refinement as fixed contributors with isotropic *U* values fixed at 0.08 Å^2. In all cases the final difference maps showed no unusual features, with no significant peak above the general background. Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using SHELX 76.[11]

Complex (**1**). Refinement was carried out first isotropically, then anisotropically only for titanium, chlorine, and oxygen atoms because of the low percentage of observed reflections, due to the poor quality of the crystals available. A toluene molecule of crystallization was found to be distributed around a centre of symmetry. Consequently the C(4S) methyl carbon was considered to be disordered and refined with a site occupancy of 0.5. All the hydrogen atoms, except those associated with toluene which were ignored were put in calculated positions. The final atomic co-ordinates are given in Table 2.

Complex (**2**). Refinement was carried out using anisotropic thermal parameters for all the non-hydrogen atoms except for three carbon atoms of a co-ordinated thf molecule that was found to be disordered. The disorder was solved considering three carbon atoms distributed over two positions [C(13)—C(15), and the corresponding primed ones]. The isotropic refinement of their site-occupation factors gave 0.43 and 0.53 respectively. During the refinement the benzene ring was treated as a regular hexagon (C–C 1.39 Å). The hydrogen atoms excluding those associated with the disordered thf, which were ignored, were put in geometrically idealized positions. The final atomic co-ordinates are given in Table 3.

Complex (**3**). Refinement was carried out first isotropically, then anisotropically for all non-hydrogen atoms. All the hydrogen atoms were located in a difference map. The final atomic co-ordinates are given in Table 4.

Complex (**4**). During the anisotropic refinement the C(25), C(26), and C(29) atoms reached rather high U_{ij} values suggesting the presence of some disorder affecting the thf molecules, but we did not succeed in solving it in terms of

Table 2. Fractional atomic co-ordinates (× 10^4) for complex (**1**)

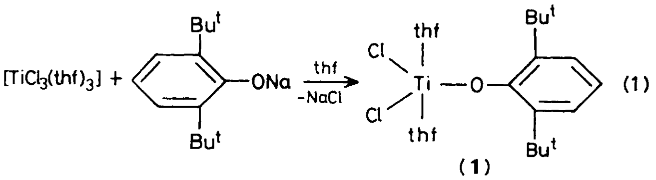
Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ti	771(2)	2 365(3)	1 400(1)	C(11)	3 713(15)	4 857(15)	1 753(6)
Cl(1)	−515(5)	4 122(4)	1 375(2)	C(12)	4 678(16)	5 930(17)	1 916(7)
Cl(2)	−511(5)	592(4)	1 385(2)	C(13)	2 870(16)	4 701(15)	2 218(7)
O(1)	2 497(7)	2 455(10)	1 425(3)	C(14)	2 925(14)	5 247(14)	1 223(6)
O(2)	824(8)	2 334(11)	2 265(4)	C(15)	−141(17)	2 883(16)	2 584(7)
O(3)	535(8)	2 372(12)	526(4)	C(16)	200(14)	2 348(18)	3 140(6)
C(1)	3 808(12)	2 458(18)	1 493(5)	C(17)	1 640(14)	2 155(15)	3 168(6)
C(2)	4 481(15)	1 386(14)	1 396(6)	C(18)	1 753(16)	1 639(15)	2 623(7)
C(3)	5 847(17)	1 431(16)	1 491(7)	C(19)	−563(22)	1 855(20)	205(9)
C(4)	6 448(13)	2 488(19)	1 678(6)	C(20)	−482(22)	2 428(25)	−344(9)
C(5)	5 793(16)	3 547(15)	1 767(7)	C(21)	743(21)	2 972(20)	−366(9)
C(6)	4 416(15)	3 590(15)	1 668(6)	C(22)	1 139(19)	3 294(19)	212(8)
C(7)	3 860(16)	159(15)	1 175(6)	C(1S)	3 989(23)	243(30)	4 648(10)
C(8)	3 073(17)	361(17)	633(7)	C(2S)	4 572(33)	1 276(31)	4 835(13)
C(9)	2 987(17)	−380(16)	1 579(7)	C(3S)	5 807(34)	981(39)	5 262(14)
C(10)	4 836(17)	−856(18)	1 091(7)	C(4S)	5 713(36)	2 065(39)	5 203(15)

Table 3. Fractional atomic co-ordinates (× 10^4) for complex (**2**)

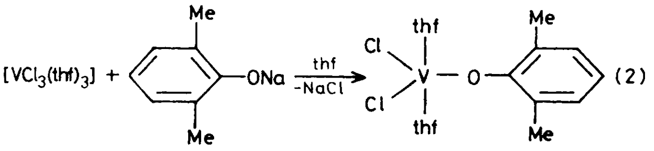
Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
V	4 487(2)	1 245(2)	1 993(1)	C(8)	6 601(17)	−604(9)	3 359(6)
Cl(1)	3 448(5)	−241(2)	1 544(2)	C(9)	1 863(18)	2 072(9)	3 062(7)
Cl(2)	3 263(5)	2 699(3)	1 564(2)	C(10)	1 677(18)	1 664(15)	3 796(7)
O(1)	6 358(8)	1 277(6)	2 646(3)	C(11)	1 623(21)	555(14)	3 744(8)
O(2)	2 530(8)	1 203(7)	2 712(3)	C(12)	1 719(18)	307(10)	2 997(6)
O(3)	6 466(10)	1 311(9)	1 289(3)	C(16)	8 405(16)	1 255(15)	1 428(5)
C(1)	6 525(8)	1 303(6)	3 328(2)	C(13)	5 883(41)	906(29)	553(15)
C(2)	6 638(8)	2 233(6)	3 665(2)	C(14)	7 737(51)	945(33)	244(19)
C(3)	6 819(8)	2 264(6)	4 376(2)	C(15)	8 942(43)	792(30)	678(16)
C(4)	6 885(8)	1 364(6)	4 749(2)	C(13′)	5 975(33)	1 645(22)	565(11)
C(5)	6 772(8)	433(6)	4 411(2)	C(14′)	7 728(50)	1 587(33)	256(19)
C(6)	6 591(8)	403(6)	3 701(2)	C(15′)	9 227(35)	1 440(25)	744(13)
C(7)	6 605(19)	3 201(8)	3 253(6)				

Table 4. Fractional atomic co-ordinates (× 10^4) for complex (**3**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
V	611(1)	312(1)	1 366(1)	C(5)	956(4)	1 908(7)	−2 678(6)
Cl	943(1)	−269(2)	3 752(2)	C(6)	925(3)	1 550(6)	−1 273(6)
O(1)	1 409(2)	1 614(5)	1 143(4)	C(7)	982(4)	−2 966(7)	1 252(8)
O(2)	361(2)	754(4)	−786(4)	C(8)	1 704(5)	−3 772(8)	1 622(9)
O(3)	1 221(2)	−1 506(4)	834(4)	C(9)	2 272(4)	−3 044(9)	843(9)
O(4)	−30(2)	2 071(4)	1 968(4)	C(10)	2 046(4)	−1 465(8)	883(8)
C(1)	1 492(3)	2 001(7)	−193(7)	C(11)	323(5)	3 450(8)	2 373(10)
C(2)	2 090(4)	2 849(7)	−537(7)	C(12)	−231(7)	4 284(11)	3 018(14)
C(3)	2 119(4)	3 244(8)	−1 943(8)	C(13)	−803(5)	3 314(9)	3 408(10)
C(4)	1 554(4)	2 761(7)	−2 990(7)	C(14)	−693(4)	1 901(8)	2 740(7)



(**1**)



(**2**)

'partial' atoms. So the anisotropic refinement was considered satisfactory. Most of the hydrogen atoms were located from a difference map, the others, particularly those associated with C(25), C(26), and C(29), were put in calculated positions. The final atomic co-ordinates are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Reaction of [TiCl$_3$(thf)$_3$] and [VCl$_3$(thf)$_3$] with the sodium salt of 2,6-Bu$^t_2$C$_6$H$_3$OH and 2,6-Me$_2$C$_6$H$_3$OH respectively led to a good yield synthesis in thf of the corresponding monophenoxo derivatives (**1**) and (**2**). Complexes (**1**) and (**2**) are very sensitive materials, which can be isolated in a crystalline form. They have magnetic moments [1.79, (**1**); 2.87, (**2**)] expected for monomeric

Table 5. Fractional atomic co-ordinates (× 10^4) for complex (**4**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
V	2 675(1)	3 031(1)	702(0)	C(16)	2 531(8)	−134(5)	668(3)
Cl	5 101(2)	3 192(2)	641(1)	C(17)	3 881(8)	307(6)	966(4)
O(1)	1 757(4)	1 898(3)	510(2)	C(18)	2 609(9)	10(6)	54(3)
O(2)	1 492(4)	4 066(3)	835(2)	C(19)	2 582(11)	−1 223(6)	791(4)
C(1)	845(6)	1 329(5)	776(3)	C(20)	1 834(8)	5 708(5)	1 587(3)
C(2)	1 158(7)	344(5)	869(3)	C(21)	3 321(8)	5 267(6)	1 707(4)
C(3)	199(8)	−199(5)	1 162(3)	C(22)	1 793(11)	6 168(6)	1 021(4)
C(4)	−1 095(8)	198(6)	1 327(3)	C(23)	1 653(9)	6 517(6)	2 001(4)
C(5)	−1 402(7)	1 158(6)	1 204(3)	O(3)	2 415(5)	3 421(3)	−125(2)
C(6)	−467(7)	1 720(4)	923(3)	C(24)	2 762(10)	2 735(6)	−543(3)
C(7)	−890(6)	2 774(5)	767(3)	C(25)	3 130(17)	3 324(9)	−1 002(4)
C(8)	−615(6)	3 513(4)	1 219(3)	C(26)	3 242(14)	4 300(8)	−851(4)
C(9)	−1 578(7)	3 573(4)	1 642(3)	C(27)	2 607(9)	4 417(6)	−305(3)
C(10)	−1 419(7)	4 258(5)	2 049(3)	O(4)	3 026(4)	2 648(3)	1 554(2)
C(11)	−301(7)	4 930(5)	2 023(3)	C(28)	4 446(7)	2 643(7)	1 856(3)
C(12)	674(7)	4 920(5)	1 612(3)	C(29)	4 131(11)	2 487(11)	2 430(4)
C(13)	542(6)	4 170(5)	1 227(3)	C(30)	2 707(11)	2 234(7)	2 457(3)
C(14)	−2 114(9)	−429(6)	1 635(4)	C(31)	2 023(8)	2 272(7)	1 916(3)
C(15)	−2 440(8)	4 307(6)	2 499(3)				

Table 6. Selected bond distances (Å) and angles (°) for complex (**1**)

Ti–Cl(1)	2.320(6)	Ti–O(2)	2.145(9)
Ti–Cl(2)	2.334(6)	Ti–O(3)	2.160(9)
Ti–O(1)	1.807(8)	O(1)–C(1)	1.37(1)
Cl(1)–Ti–Cl(2)	109.6(2)	Cl(1)–Ti–O(1)	122.3(4)
Cl(2)–Ti–O(1)	128.1(4)	Cl(1)–Ti–O(2)	89.8(3)
Cl(2)–Ti–O(2)	87.8(3)	O(1)–Ti–O(2)	92.2(4)
Cl(1)–Ti–O(3)	87.8(3)	Cl(2)–Ti–O(3)	88.7(3)
O(1)–Ti–O(3)	92.9(4)	O(2)–Ti–O(3)	174.9(4)
Ti–O(1)–C(1)	174.2(9)		

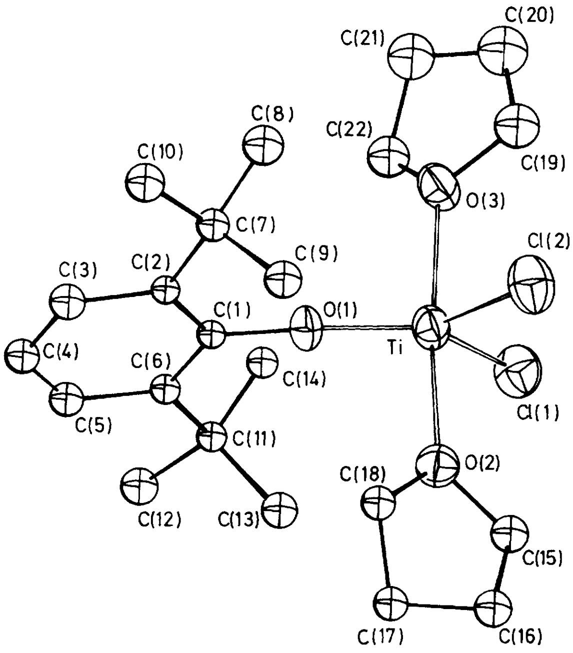


Figure 1. An ORTEP drawing of complex (**1**)

d^1 and d^2 complexes. The presence of two chloride ligands in both complexes makes the metal atom easily reducible and functionalizable. The structure has been determined by an *X*-ray analysis.

Table 7. Selected bond distances (Å) and angles (°) for complex (**2**)

V–Cl(1)	2.259(4)	V–O(2)	2.095(5)
V–Cl(2)	2.253(4)	V–O(3)	2.087(7)
V–O(1)	1.803(5)	O(1)–C(1)	1.338(6)
Cl(1)–V–Cl(2)	118.7(1)	Cl(1)–V–O(1)	120.8(3)
Cl(2)–V–O(1)	120.3(3)	Cl(1)–V–O(2)	90.1(2)
Cl(2)–V–O(2)	90.1(2)	O(1)–V–O(2)	92.4(2)
Cl(1)–V–O(3)	90.9(2)	Cl(2)–V–O(3)	89.6(2)
O(1)–V–O(3)	89.6(2)	O(2)–V–O(3)	178.8(3)
V–O(1)–C(1)	135.9(5)		

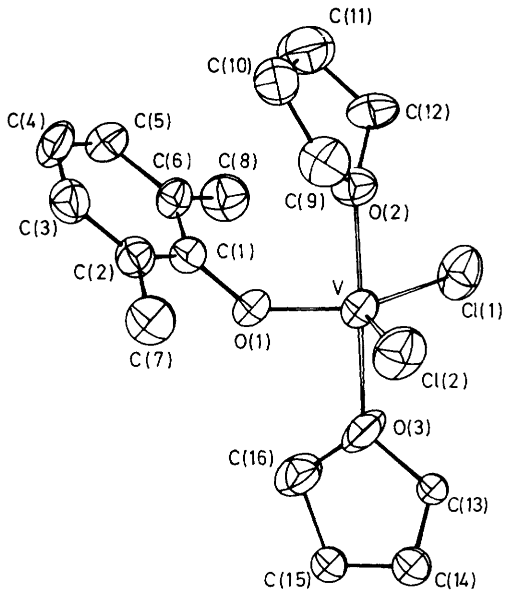


Figure 2. An ORTEP drawing of complex (**2**). The disorder affecting the C(13)—C(15) carbon atoms is not shown for clarity

The structure of (**1**) is shown in Figure 1, while a selection of bond distances and angles is reported in Table 6. Titanium has a pseudo-trigonal-bipyramidal co-ordination, the equatorial plane being defined by Ti, Cl(1), Cl(2), O(1). The titanium atom is out by 0.230(3) Å from the plane of the phenyl ring which forms a

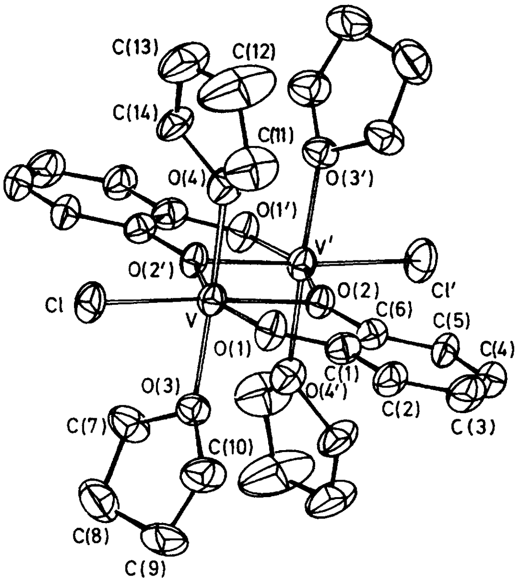


Figure 3. An ORTEP drawing of the dimeric complex (**3**). Prime indicates the transformation $-x, -y, -z$

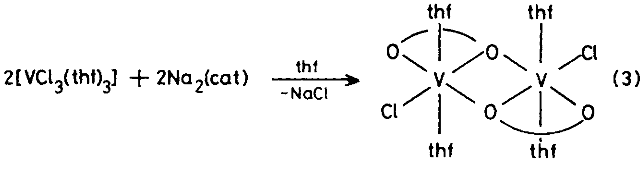
Table 8. Selected bond distances (Å) and angles (°) for complex (**3**)*

V–Cl	2.336(2)	O(1)–C(1)	1.348(8)
V–O(1)	1.890(4)	O(2)–C(6)	1.370(7)
V–O(2)	2.081(4)	O(3)–C(7)	1.483(8)
V–O(2′)	2.001(4)	O(3)–C(10)	1.459(8)
V–O(3)	2.095(4)	O(4)–C(11)	1.450(9)
V–O(4)	2.105(4)	O(4)–C(14)	1.473(8)
O(3)–V–O(4)	177.1(2)	Cl–V–O(2)	176.9(1)
O(2′)–V–O(4)	88.8(2)	Cl–V–O(1)	99.0(1)
O(2′)–V–O(3)	89.6(2)	V–O(2)–V′	104.1(2)
O(2)–V–O(4)	93.6(2)	V–O(1)–C(1)	116.7(4)
O(2)–V–O(3)	88.3(2)	V′–O(2)–C(6)	144.3(3)
O(2′)–V–O(2)	76.0(2)	V–O(2)–C(6)	111.5(3)
O(1)–V–O(4)	88.7(2)	V–O(3)–C(10)	121.2(4)
O(1)–V–O(3)	93.8(2)	V–O(3)–C(7)	119.3(4)
O(2′)–V–O(1)	156.0(2)	C(7)–O(3)–C(10)	109.6(5)
O(1)–V–O(2)	80.4(2)	V–O(4)–C(14)	123.2(4)
Cl–V–O(4)	89.5(1)	V–O(4)–C(11)	121.4(4)
Cl–V–O(3)	88.7(1)	C(11)–O(4)–C(14)	107.8(5)
Cl–V–O(2′)	104.9(1)		

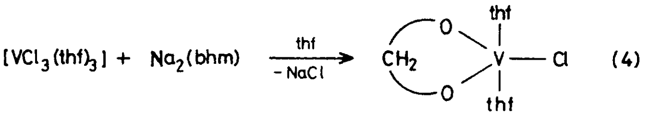
* Prime (′) indicates the transformation $-x, -y, -z$.

dihedral angle of 17.9(4)° with the equatorial plane. The Ti–O distances vary from a short one 1.807(8) Å [Ti–O(1)] to much longer values [Ti–O(2) 2.145(9), Ti–O(3) 2.160(9) Å] for those involving thf molecules. The Ti–O(phenoxide) distance is significantly shorter than the value found in $[\mathrm{Ti}(\eta^5\text{-}C_5H_5)_2(2,6\text{-}Bu^t_2\text{-}4\text{-}MeC_6H_2O)]$[15] [1.892(2) Å]. The Ti–O(1) bond distance along with the value of the Ti–O(1)–C(1) angle [174.2(9)°] supports a Ti–O multiple bond, with an oxygen having a nearly *sp* hybridization. The two Ti–Cl bond distances [Ti–Cl(1) 2.320(6), Ti–Cl(2) 2.334(6) Å] are not significantly different. Vanadium in complex (**2**) has a co-ordination geometry similar to that of titanium in (**1**). The structure is shown in Figure 2, with a selection of bond distances and angles in Table 7. The most significant differences from the structure of complex (**1**) are: (*i*) the deviation [0.041(2) Å] of vanadium from the equatorial plane defined by O(1), Cl(1), Cl(2), and from the plane of the phenyl ring [1.249(2) Å]; (*ii*) the V–O(1) bond distance [1.803(5) Å] and the V–O(1)–C(1) angle [135.9(5)°] showing a smaller metal–oxygen interaction with an oxygen atom approaching sp^2 hybridization. By consequence the reciprocal orientation of the phenyl ring and the equatorial plane is much different, the dihedral angle being 42.8(1)°. The V–O(phenoxide) and V–Cl bond distances are in the range observed for $[V_2\{OC_6H_4(OMe)\text{-}2\}_4Cl_2]$[5], $[V_2(\mu\text{-cat})_2Cl_2(thf)_4]$, (**3**), and $[V(bhm)Cl(thf)_2]$, (**4**).

Reaction of $[VCl_3(thf)_3]$ with $Na_2(cat)$ and $Na_2(bhm)$ afforded complexes (**3**) and (**4**), with a partial substitution of the chloride ion. A stoicheiometric ligand:metal ratio was used in reaction (3) to produce a vanadium centre susceptible to reduction or functionalization. The relatively high yield of (**3**) shows that there is no significant ligand-disproportionation reaction leading to by-products. Complex (**3**) has a normal magnetic moment of 2.86 per vanadium at room temperature, without any magnetic coupling between the two close vanadium atoms. The *X*-ray structure shows that the skeleton of (**3**) is planar with labile molecules of solvent above and below. This is an important structural feature for the use of (**3**) in chemical reactivity studies.



$[V_2(\mu\text{-cat})_2Cl_2(thf)_4]$, (**3**)



$[V(bhm)Cl(thf)_2]$, (**4**)

The use of the diphenol H_2bhm was suggested by the necessity to provide a rather hindered co-ordination environment around vanadium in order to produce a mononuclear complex. In addition, the imposed geometrical proximity of the bridging CH_2 with the metal may be of relevance in further reactivity studies. The structure of complex (**4**) has been determined by an *X*-ray analysis (see below). The magnetic moment has the expected value for a d^2 system (2.80 at 293 K). The significant difference between complexes (**3**) and (**4**), excluding molecular complexity, is the solubility, complex (**4**) being very soluble even in hydrocarbons.

Complex (**3**) is shown in Figure 3, selected bond distances and angles being quoted in Table 8. The structure consists of centrosymmetric $[V_2(\mu\text{-cat})_2Cl_2(thf)_4]$ dimers where each vanadium exhibits a pseudo-octahedral co-ordination involving a chlorine atom, two oxygen atoms from thf molecules, and two oxygen atoms from a catecholato anion behaving as a chelating ligand; moreover the O(2) oxygen atom bridges the centrosymmetric vanadium atom giving rise to the dimer. The V ··· V′ distance [3.218(2) Å] rules out any possible metal–metal interaction. The bite angle [O(1)–V–O(2) 80.4(2)°] and the bridge angles [O(2)–V–O(2′), 76.0(2), V–O(2)–V′ 104.1(2)°] are very similar to those found in the related complex $[V_2\{OC_6H_4(OMe)\text{-}2\}_4Cl_2]$.[5] This bonding mode is mainly responsible for the distortion of the co-ordination polyhedron. The V–O and V–Cl bond distances agree well with the corresponding ones in $[V_2\{OC_6H_4(OMe)\text{-}2\}_4Cl_2]$[5] and in $[V(cat)_3]^{3-}$.[16] The bridge is slightly asymmetrical with the two V–O distances [V–O(2) 2.081(4), V–O(2′) 2.001(4) Å] being significantly different. The

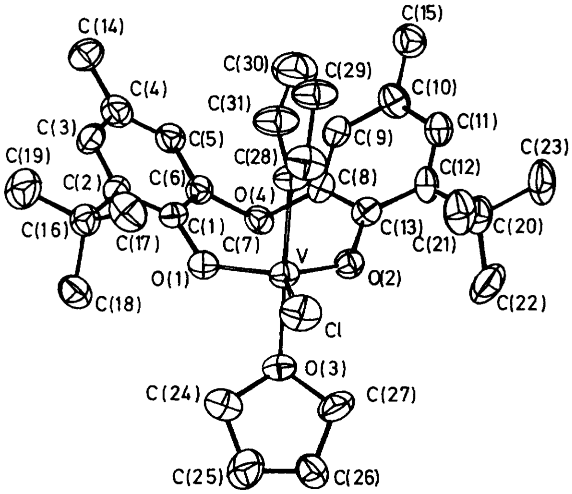


Figure 4. An ORTEP drawing of complex (**4**)

Table 9. Selected bond distances (Å) and angles (°) for complex (**4**)

V–Cl	2.288(2)	O(1)–C(1)	1.356(8)
V–O(1)	1.832(4)	O(2)–C(13)	1.356(8)
V–O(2)	1.847(4)	O(3)–C(24)	1.449(9)
V–O(3)	2.102(5)	O(3)–C(27)	1.460(9)
V–O(4)	2.165(5)	O(4)–C(28)	1.478(8)
C(6)–C(7)	1.550(9)	O(4)–C(31)	1.428(9)
C(7)–C(8)	1.519(10)		
O(3)–V–O(4)	177.8(2)	Cl–V–O(1)	121.0(2)
O(2)–V–O(4)	94.3(2)	V–O(1)–C(1)	132.0(4)
O(2)–V–O(3)	86.5(2)	V–O(2)–C(13)	129.1(4)
O(1)–V–O(4)	94.6(2)	V–O(3)–C(27)	121.7(4)
O(1)–V–O(3)	86.9(2)	V–O(3)–C(24)	120.0(4)
O(1)–V–O(2)	115.6(2)	C(24)–O(3)–C(27)	111.4(5)
Cl–V–O(4)	89.8(1)	V–O(4)–C(31)	128.7(4)
Cl–V–O(3)	88.1(2)	V–O(4)–C(28)	124.4(4)
Cl–V–O(2)	122.7(2)	C(28)–O(4)–C(31)	106.7(5)

V_2O_2 core is strictly planar for symmetry requirements, O(1) and Cl being out of it by 0.132(4) and 0.121(2) Å respectively on opposite sides. It forms a dihedral angle of 5.5° with the catecholato ligand which is planar within experimental errors. Vanadium lies 0.189(1) Å from this plane. These values indicate an approximate planarity of the dimeric skeleton $V_2(\mu\text{-cat})_2Cl_2$. All the other bond distances and angles are as expected. There are no intermolecular contacts other than van der Waals interactions.

Complex (**4**) is shown in Figure 4, selected bond distances and angles being quoted in Table 9. The structure consists of discrete monomeric [V(bhm)Cl(thf)$_2$] molecules. Vanadium is surrounded by a chlorine atom, two oxygen atoms from thf molecules, and two oxygen atoms from a bhm molecule behaving as a chelating ligand. The resulting eight-membered chelation ring is puckered, vanadium lying 1.216(1) and 1.334(1) Å from the planes through the group of atoms O(1), C(1), C(6), C(7) and O(2), C(13), C(8), C(7) respectively. These planes form a dihedral angle of 62.3(3)°. The polyhedron co-ordination can be described as a trigonal bipyramid. The atoms in the equatorial plane are not strictly coplanar, vanadium lying 0.097(1) Å from the plane through O(1), O(2), Cl. The distortion, as well as the significant difference between the V–O(3) and V–O(4) distances, respectively 2.102(5) and 2.165(5) Å, could be due to intraligand steric interactions. The V–O and V–Cl distances in the equatorial plane [V–O(1) 1.832(4), V–O(2) 1.847(4), V–Cl 2.288(2) Å] are significantly shorter than those found in complex (**3**) and in $[V_2(cat)_2Cl_2]$[5] and $[V(cat)_3]^{3-}$,[16] as a consequence of the decreased co-ordination number. Bond distances and angles in the bhm ligands are as expected, the dihedral angle between the two aromatic moieties being 58.8(1)°. The CH_2 bridge is not involved in a direct interaction with the metal, the V • • • C(7) and V • • • H(71) distances being 3.358(6) and 2.90 Å respectively. It is quite clear, however, that such a C–H unit is predetermined for a reaction with the metal centre.

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References

1 A. J. Edwards, in 'Comprehensive Coordination Chemistry,' eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, ch. 30, pp. 333—334.
2 A. Flamini, D. J. Cole-Hamilton, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 454.
3 E. E. van Tamelen, *Acc. Chem. Res.*, 1970, **3**, 361.
4 S. A. Isaeva and L. A. Nikonova, *Izv. Akad. Nauk. SSSR*, 1977, 1968; N. P. Luneva, L. A. Nikonova, and A. E. Shilov, *Kinet. Katal.*, 1977, **18**, 254, 1980, **21**, 1041; N. P. Luneva, A. P. Moravsky, and A. E. Shilov, *Nouv. J. Chim.*, 1982, **21**, 245; G. N. Schrauzer and M. R. Palmer, *J. Am. Chem. Soc.*, 1981, **103**, 2659; R. A. Henderson, G. J. Leigh; and C. J. Pickett, *Adv. Inorg. Chem. Radiochem.*, 1983, **27**, 197.
5 M. Mazzanti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 576.
6 M. T. Reetz, *Top. Curr. Chem.*, 1982, **106**, 1; T. V. Lubben and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1985, **107**, 701; A. K. McMullen, I. P. Rothwell, and J. C. Huffman, *ibid.*, p. 1072; S. L. Latesky, A. K. McMullen, G. P. Niccolai, and I. P. Rothwell, *Organometallics*, 1985, **4**, 902, 995; J. L. Kerschner, P. E. Fanwick, and I. P. Rothwell, *J. Am. Chem. Soc.*, 1987, **109**, 5840 and refs. therein; L. R. Chamberlain, J. L. Kerschner, A. P. Rothwell, I. P. Rothwell, and J. C. Huffman, *ibid.*, p. 6471.
7 A. W. Duff, R. A. Kamarudin, M. F. Lappert, and R. J. Norton, *J. Chem. Soc., Dalton Trans.*, 1986, 489.
8 L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 135.
9 S. L. Lawton and R. A. Jacobson, 'TRACER', a cell-reduction program, Ames Laboratory, Iowa State University of Science and Technology, 1965.
10 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
11 G. M. Sheldrick, SHELX 76, System of Crystallographic Computer Programs, University of Cambridge, 1976.
12 A. J. C. Wilson, *Nature* (*London*), 1942, **150**, 151.
13 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, (*a*) p. 149, (*b*) p. 99.
14 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
15 B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, S. Torroni, J. L. Atwood, W. E. Hunter, and M. J. Zaworotko, *J. Organomet. Chem.*, 1980, **188**, C31.
16 S. R. Cooper, Y. B. Koh, and K. N. Raymond, *J. Am. Chem. Soc.*, 1982, **104**, 5092.

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