Synthesis and Characterization of New Di- and Tetra-meric Vanadium Intermediates of Olefin Polymerization Catalysts. Crystal Structures of $[V_2(\mu\text{-}Cl)_2Cl_4(MeCO_2Et)_4]$ and $[\{VOCl_2[CH_2(CO_2Et)_2]\}_4]\cdot 2CH_2Cl_2$†

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The direct reaction of VCl_3 and ethyl acetate yields $[V_2(\mu\text{-}Cl)_2Cl_4(MeCO_2Et)_4]$ **1**. The compound $[V_2(\mu\text{-}Cl)_2Cl_4\{CH_2(CO_2Et)_2\}_2]$ **2** was obtained in dichloromethane *via* the substitution of $MeCO_2Et$ in **1** by ethyl malonate. During crystallization of **2**, under the influence of dioxygen and moisture, the tetrameric compound $[\{VOCl_2[CH_2(CO_2Et)_2]\}_4]\cdot 2CH_2Cl_2$ **3** was formed. The crystal structures of **1** and **3** have been determined by single-crystal X-ray diffraction studies. The dimeric compound **1** exhibits six-co-ordinate V^{III} centres [separated by a V···V distance of 3.590(1) Å] surrounded by two terminal Cl atoms, two carbonyl oxygen atoms of co-ordinated ethyl acetate molecules and linked by two bridging Cl atoms. In the tetrameric species **3**, the four vanadium(IV) atoms have equivalent octahedral geometries, being bonded by two mutually *cis* chlorine atoms, two mutually *cis* carbonyl oxygen atoms of chelate ethyl malonate and two mutually *cis* oxygen atoms. High catalytic activity was found for **1**, **2** and $[V_2(\mu\text{-}Cl)_2Cl_4(thf)_4]$ (thf = tetrahydrofuran).

Supported titanium and vanadium α-olefin polymerization catalysts, in the presence of $AlEt_3$ and halogenocarbons as promoters, display high activity.[1] The behaviour of these catalysts can be controlled by addition of Lewis base. In some cases the addition of electron-donor species leads to a significant increase in catalytic activity. Therefore ether or ester complexes of early transition metals are of great interest. Among the electron-donor compounds studied with vanadium catalysts were oxygen-containing species such as organic ethers or esters.[1] During the last several years we have obtained a family of new titanium-(IV) and -(III) complexes with mono- and di-esters of carboxylic acids.[2] Some of them were used as precursors for the preparation of Ziegler–Natta type catalysts for α-olefin polymerization.[3] Although many vanadium-(II) and -(III) complexes with organic ethers are known,[4] no vanadium compounds with esters of carboxylic acids have been reported until now.

We describe here a new simple high-yield method of synthesis leading to dimeric vanadium(III) complexes $[V_2(\mu\text{-}Cl)_2Cl_4(MeCO_2Et)_4]$ **1** and $[V_2(\mu\text{-}Cl)_2Cl_4\{CH_2(CO_2Et)_2\}_2]$ **2** and tetrameric vanadium(IV) $[\{VOCl_2[CH_2(CO_2Et)_2]\}_4]\cdot 2CH_2Cl_2$ **3** ester compounds.

Results and Discussion

Synthesis and Structure of $[V_2(\mu\text{-}Cl)_2Cl_4(MeCO_2Et)_4]$ **1**.—The direct reaction of VCl_3 with ethyl acetate leads to the formation of the vanadium(III) compound **1** [equation (1)].

$$2VCl_3 + 4MeCO_2Et \longrightarrow \underset{\mathbf{1}}{[V_2(\mu\text{-}Cl)_2Cl_4(MeCO_2Et)_4]} \quad (1)$$

The reaction was carried out using Soxhlet extraction of VCl_3 with boiling ethyl acetate following the well known preparative method for $[VCl_3(thf)_3]$ (thf = tetrahydrofuran).[5] When the brown solution of **1** was exposed to slow diffusion of *n*-hexane a deep red, needle-shaped crystalline solid of composition $VCl_3\cdot 2MeCO_2Et$ **1** was formed. Compound **1** is very unstable, immediately decomposing on exposure either to air or moisture, but is stable under N_2. The IR spectrum shows bands due to ester ν(C=O) group and broad bands at 310s and 356vs cm^{-1} attributed to ν(V–Cl). The complex as a solid shows bands at 12 800 and 23 500 cm^{-1} in its diffuse reflectance spectrum, close to the values of 12 250 and 20 200 cm^{-1} observed in $MeCO_2Et$. Those bands can be assigned to the $^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$ transition, respectively, for co-ordinated d^2 species, *cf.* $[V_2(\mu\text{-}Cl)_2Cl_4(thf)_4]$,[6] $[VCl_2(H_2O)_4]Cl$,[7] $[VCl_2(ROH)_4]Cl$[8] (R = alkyl) and $[VCl_2(MeCN)_4][SbCl_6]$.[9] The electronic spectra suggest that the complex has similar structure in solution and in the solid state.

Table 1 lists selected bond lengths and angles for compound **1**. In the crystalline state compound **1** is composed of discrete molecules of $[V_2(\mu\text{-}Cl)_2Cl_4(MeCO_2Et)_4]$ (Fig. 1). The molecule consists of two somewhat distorted octahedra sharing a common edge. Each vanadium(III) atom is octahedrally co-ordinated by two terminal chlorine atoms, two bridging chlorine atoms and two oxygen atoms of two carbonyl groups of the ethyl acetate ligands. The two $MeCO_2Et$ molecules are co-ordinated to vanadium atoms *via* the carbonyl oxygen atoms and are in *cis* orientation. The general structure of the dimeric molecule **1** is similar to that of $[V_2(\mu\text{-}Cl)_2Cl_4(thf)_4]$.[6] The O(3) atom of the carbonyl group of the ethyl acetate molecule is situated *trans* and *cis* to the bridging chlorine atoms Cl(1′) and Cl(1), respectively, while O(1) of the second $MeCO_2Et$ molecule is *cis* to both bridging chlorine atoms. The V–Cl$_b$ bond lengths of 2.441(2) and 2.415(2) Å are similar to V–Cl$_b$ of 2.424(1), 2.440(1) and 2.477(1) Å in $[V_2(\mu\text{-}Cl)_2Cl_4(thf)_4]$[6] and $[V_2(\mu\text{-}Cl)_3(thf)_6]^+$.[10] The terminal V–Cl and V–O distances

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

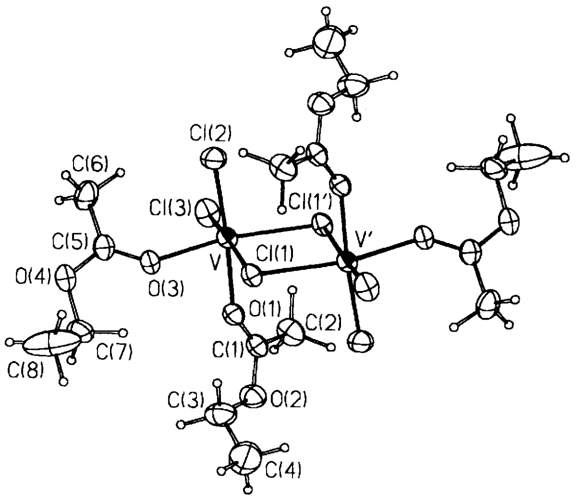


Fig. 1 Structure and the numbering scheme for complex **1**

Table 1 Selected bond lengths (Å), bond angles (°) and torsion angles (°) for complex **1** *

V–V'	3.590(1)	V–O(1)	2.038(4)
V–Cl(1)	2.441(2)	V–O(2)	2.053(4)
V–Cl(1')	2.415(2)	O(1)–C(1)	1.216(9)
V–Cl(2)	2.268(2)	O(3)–C(5)	1.218(8)
V–Cl(3)	2.269(2)		
V–Cl(1)–V'	95.3(1)	Cl(1')–V–O(1)	91.4(2)
Cl(1)–V–Cl(1')	84.7(1)	Cl(1')–V–O(3)	169.5(2)
Cl(1)–V–Cl(2)	90.3(1)	Cl(2)–V–Cl(3)	96.8(1)
Cl(1)–V–Cl(3)	172.8(1)	Cl(2)–V–O(1)	170.2(2)
Cl(1)–V–O(1)	81.9(2)	Cl(2)–V–O(3)	93.2(2)
Cl(1)–V–O(3)	87.4(2)	Cl(3)–V–O(1)	91.2(2)
Cl(1')–V–Cl(2)	93.8(1)	Cl(3)–V–O(3)	93.2(2)
Cl(1')–V–Cl(3)	93.8(1)	O(1)–V–O(3)	80.6(2)
V–O(1)–C(1)–O(2)	165.3(9)	V–O(3)–C(5)–C(6)	1.2(10)
V–O(1)–C(1)–C(2)	−16.1(9)	O(1)–C(1)–O(2)–C(3)	−2.6(8)
V–O(3)–C(5)–O(4)	−177.9(9)	O(3)–C(5)–O(4)–C(7)	0.7(9)

* Primed atoms are related to unprimed atoms by $-x, 1-y, -z$.

as well as the O–V–O, Cl–V–Cl and V–Cl$_b$–V bond angles are close to the corresponding values in dimeric [V$_2$(μ-Cl)$_2$Cl$_4$(thf)$_4$].[6]

Compound **1** is paramagnetic with a temperature independent (4.2–293 K) μ_{eff} of 2.72 μ_B per vanadium atom (a plot of $1/\chi$ *vs.* T gives a straight line passing through the origin). No EPR signal was observed in the solid state, which additionally confirms the vanadium(III) oxidation state ($S = 1$).

Synthesis and Properties of [V$_2$(μ-Cl)$_2$Cl$_4${CH$_2$(CO$_2$Et)$_2$}$_2$] **2**.—The addition of 2 equivalents of diethyl malonate to **1** in toluene–dichloromethane (1 : 1) results in the formation of an air-sensitive, brown compound of composition VCl$_3$·CH$_2$(CO$_2$Et)$_2$ **2** [equation (2)] which can be stored under

$$\underset{\mathbf{1}}{[V_2(\mu\text{-Cl})_2Cl_4(MeCO_2Et)_4]} + 2CH_2(CO_2Et)_2 \longrightarrow \underset{\mathbf{2}}{[V_2(\mu\text{-Cl})_2Cl_4\{CH_2(CO_2Et)_2\}_2]} + 4MeCO_2Et \quad (2)$$

dinitrogen. It is insoluble in halogeno- and hydro-carbon solvents.

The IR spectrum of **2** shows the expected bands due to carbonyl oxygen co-ordinated diester ethyl malonate molecules [ν(C=O) at 1622m and 1672vs cm^{-1}] and bands at 300 (sh), 346vs, 390m cm^{-1} attributed to ν(V–Cl). The complex as a solid, like **1**, shows bands at 14 920 and 22 470 cm^{-1} in its diffuse reflectance spectrum which are close to the values of 14 500 and 21 450 cm^{-1} observed in CH$_2$Cl$_2$ solution, typical for d^2-transitions.

Compound **2** is paramagnetic with a temperature-independent (4.2–293 K) μ_{eff} of 2.62 μ_B per vanadium atom (a plot of $1/\chi$ *vs.* T gives a straight line passing through the origin). No EPR signal was observed in the solid state. The elemental analysis, IR and electronic spectra, magnetic properties of **2** and crystal structure of **1** suggested that compound **2** was a dimeric species [V$_2$(μ-Cl)$_2$Cl$_4${CH$_2$(CO$_2$Et)$_2$}$_2$] similar to the titanium(III) dimeric compound [Ti$_2$(μ-Cl)$_2$Cl$_4${C$_6$H$_4$(CO$_2$Et)$_2$}$_2$].[11] It follows that in the formation of **2** the ethyl acetate molecules of **1** undergo substitution by ethyl malonate. Attempts to prepare **2** in a form suitable for X-ray investigations failed, owing to its sparing solubility.

Synthesis and Structure of [{VOCl$_2$[CH$_2$(CO$_2$Et)$_2$]}$_4$]·2CH$_2$Cl$_2$ **3**.—The post-reaction mixture from the formation of **2** was filtered, leaving undissolved compound **2**, and the filtrate was left to crystallize at 273 K. Over a period of several days the colour changed from brown to deep red and a small amount of deep red cubic crystals of composition VOCl$_2$·CH$_2$(CO$_2$Et)$_2$ **3** containing vanadyl oxygen were formed. The dioxygen and moisture leaked into the vessel because the solvent had washed out the grease on the stopper. The crystallization process could be accelerated by passing dioxygen over the solution in the vessel. The formation of compound **3** must be accompanied by formation of other products, but we have been unable to detect these. We do note that the transformation was readily reproducible. The IR spectrum shows a band at 930s cm^{-1} due to [ν_{asym}(V=O→V)] and bands at 341s, 364s, 402s cm^{-1} [ν(V–Cl)] and at 1024m, 1644vs cm^{-1} attributed to [ν(C=O)] of co-ordinated ethyl malonate. The [ν_{asym}(V=O→V)] value in **3** is close to ν(V=O) 916 cm^{-1} observed in the polymeric salt [{V(salen)OV(salen)}$_2$O][BPh$_4$] [H$_2$salen = *N,N'*-bis(salicylidene)ethylenediamine].[12] A solution of **3** in CH$_2$Cl$_2$ has a hyperfine EPR spectrum with sets of eight lines arising from interaction of the d^1 electron with a ^{51}V nucleus ($I = \frac{7}{2}$) being observed. Comparison of the spectral parameters of **3** with those of VO^{2+} complexes[13] suggested that V^{III} in **2** was oxidized by dioxygen in dichloromethane to V^{IV}.[14] The compounds VCl$_3$ or [VCl(salen)] undergo oxidation by O$_2$ to V^{IV} with the intermediate formation of dioxygen adducts.[15] These are involved in the catalysis of oxygenation of *e.g.* 3,5-di-*tert*-butylpyrocatechol.[16] When **2** was dissolved in toluene–dichloromethane and the solution was stirred under O$_2$ the colour changed from brown to black, and a deep brown product was obtained [equation (3)]. The IR spectrum shows

$$\underset{\mathbf{2}}{2[V_2(\mu\text{-Cl})_2Cl_4\{CH_2(CO_2Et)_2\}_2]} \xrightarrow{+2O_2,\ -4Cl^-} \underset{\mathbf{3}}{[\{VOCl_2[CH_2(CO_2Et)_2]\}_4]} \quad (3)$$

the expected band due to ν(V=O→V) at 930 cm^{-1} and a sharp band at 984m cm^{-1} suggesting the product to be a mixture of **3** and other unidentified vanadium species.

The structure of **3**, shown in Fig. 2 with atom labelling, consists of discrete molecules of the tetramer [{VOCl$_2$[CH$_2$(CO$_2$Et)$_2$]}$_4$] together with two solvent CH$_2$Cl$_2$ molecules. Selected bond lengths and angles are given in Table 2. The four [VOCl$_2${CH$_2$(CO$_2$Et)$_2$}] units are linked by vanadyl oxygen atoms. Within the tetrameric moiety the four vanadium atoms have equivalent octahedral geometries being bonded to two mutually *cis* chlorine atoms, two mutually *cis* carbonyl oxygen atoms of the chelate ethyl malonate molecule and two mutually *cis* oxygen atoms. The V$_4$O$_4$ unit is significantly distorted from planarity. The four oxygen atoms are planar to within 0.073 Å but the vanadium atoms are *ca.* 0.16 Å alternately above and below this plane. The four V–O–V angles range from 171.2(3) to 174.0(4)°. The four V=O bond distances differ somewhat [1.621(5)–1.634(4) Å], but are slightly longer than for isolated

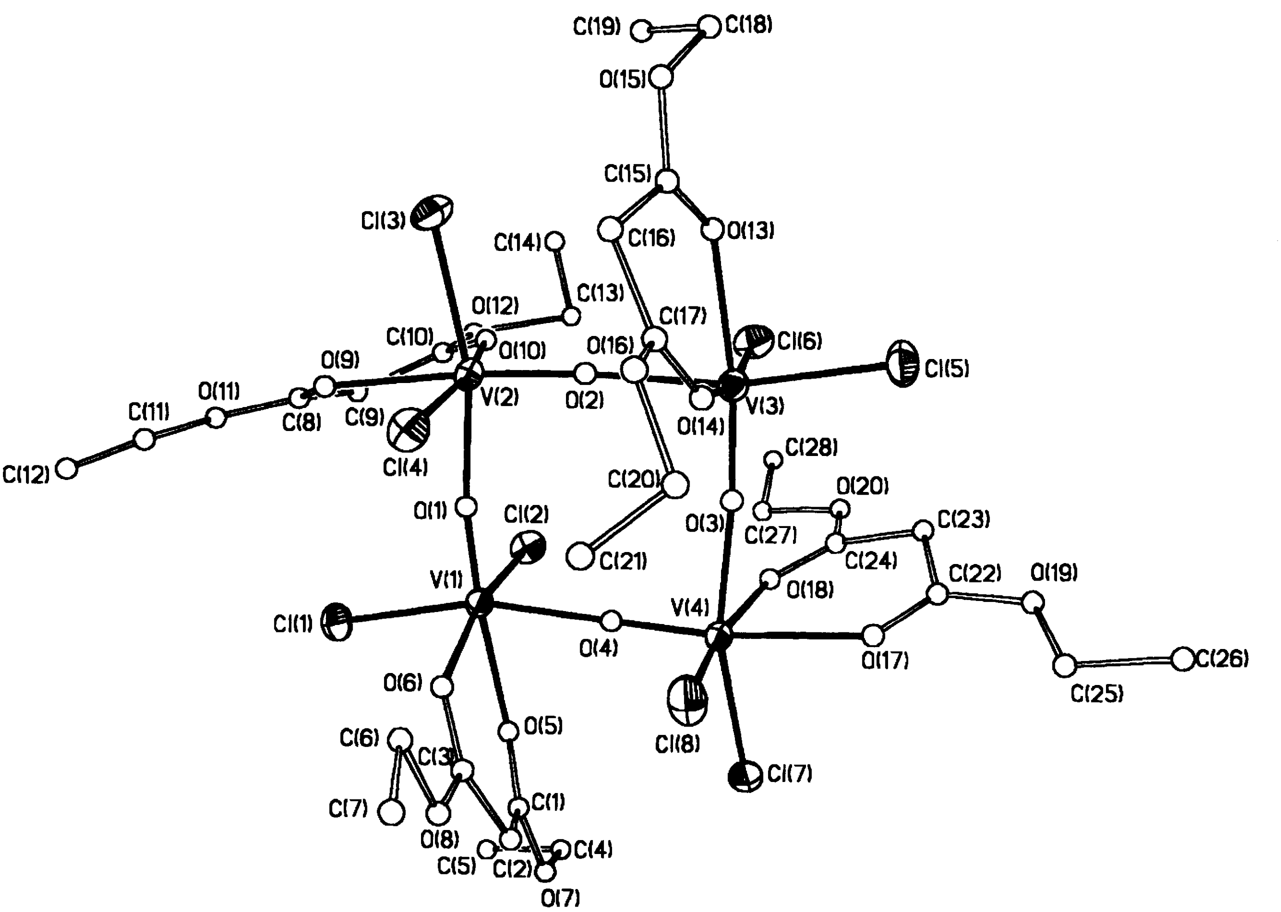


Fig. 2 Structure and numbering scheme for complex 3; H atoms are omitted for clarity

Table 2 Selected bond lengths (Å), bond angles (°) and torsion angles (°) for complex 3

V(1)–Cl(1)	2.303(2)	V(2)–Cl(3)	2.312(3)	V(3)–Cl(5)	2.310(2)	V(4)–Cl(7)	2.307(3)
V(1)–Cl(2)	2.304(2)	V(2)–Cl(4)	2.300(2)	V(3)–Cl(6)	2.294(2)	V(4)–Cl(8)	2.290(3)
V(1)–O(4)	2.024(4)	V(2)–O(1)	2.049(5)	V(3)–O(2)	2.050(5)	V(4)–O(3)	2.041(5)
V(1)–O(1)	1.621(5)	V(2)–O(2)	1.626(2)	V(3)–O(3)	1.625(5)	V(4)–O(4)	1.634(4)
V(1)–O(5)	2.177(6)	V(2)–O(9)	2.173(5)	V(3)–O(13)	2.172(6)	V(4)–O(17)	2.175(5)
V(1)–O(6)	2.080(5)	V(2)–O(10)	2.070(5)	V(3)–O(14)	2.052(5)	V(4)–O(18)	2.052(5)
O(5)–C(1)	1.228(10)	O(9)–C(8)	1.229(9)	O(13)–C(15)	1.246(10)	O(17)–C(22)	1.208(9)
O(6)–C(3)	1.214(10)	O(10)–C(10)	1.229(9)	O(14)–C(17)	1.231(11)	O(18)–C(24)	1.197(9)
Cl(1)–V(1)–Cl(2)	93.8(1)	Cl(3)–V(2)–Cl(4)	94.0(1)	Cl(5)–V(3)–Cl(6)	93.5(1)	Cl(7)–V(4)–Cl(8)	94.8(1)
Cl(1)–V(1)–O(1)	100.1(2)	Cl(3)–V(2)–O(1)	163.6(2)	Cl(5)–V(3)–O(2)	165.7(2)	Cl(7)–V(4)–O(3)	164.9(2)
Cl(1)–V(1)–O(4)	164.7(2)	Cl(3)–V(2)–O(2)	99.6(2)	Cl(5)–V(3)–O(3)	99.3(2)	Cl(7)–V(4)–O(4)	98.4(2)
Cl(1)–V(1)–O(5)	86.9(2)	Cl(3)–V(2)–O(9)	86.4(2)	Cl(5)–V(3)–O(13)	86.9(2)	Cl(7)–V(4)–O(17)	86.5(2)
Cl(1)–V(1)–O(6)	88.4(2)	Cl(3)–V(2)–O(10)	87.6(2)	Cl(5)–V(3)–O(14)	87.8(2)	Cl(7)–V(4)–O(18)	88.1(2)
Cl(2)–V(1)–O(1)	98.4(2)	Cl(4)–V(2)–O(1)	90.0(2)	Cl(6)–V(3)–O(2)	90.7(2)	Cl(8)–V(4)–O(3)	90.0(2)
Cl(2)–V(1)–O(4)	90.4(2)	Cl(4)–V(2)–O(2)	99.5(2)	Cl(6)–V(3)–O(3)	99.0(2)	Cl(8)–V(4)–O(4)	98.8(2)
Cl(2)–V(1)–O(5)	87.9(2)	Cl(4)–V(2)–O(9)	87.2(2)	Cl(6)–V(3)–O(13)	88.2(2)	Cl(8)–V(4)–O(17)	88.2(2)
Cl(2)–V(1)–O(6)	167.7(2)	Cl(4)–V(2)–O(10)	166.6(2)	Cl(6)–V(3)–O(14)	167.7(2)	Cl(8)–V(4)–O(18)	167.1(2)
O(1)–V(1)–O(4)	93.9(3)	O(1)–V(2)–O(2)	95.4(3)	O(2)–V(3)–O(3)	93.5(3)	O(3)–V(4)–O(4)	95.0(3)
O(1)–V(1)–O(5)	170.2(3)	O(1)–V(2)–O(9)	77.9(2)	O(2)–V(3)–O(13)	79.6(2)	O(3)–V(4)–O(17)	79.3(2)
O(1)–V(1)–O(6)	93.1(3)	O(1)–V(2)–O(10)	85.0(2)	O(2)–V(3)–O(14)	85.3(2)	O(3)–V(4)–O(18)	84.3(2)
O(4)–V(1)–O(5)	78.5(2)	O(2)–V(2)–O(9)	170.6(3)	O(3)–V(3)–O(13)	170.2(3)	O(4)–V(4)–O(17)	171.1(3)
O(4)–V(1)–O(6)	84.5(2)	O(2)–V(2)–O(10)	93.3(3)	O(3)–V(3)–O(14)	92.9(3)	O(4)–V(4)–O(18)	93.2(3)
O(5)–V(1)–O(6)	80.1(2)	O(9)–V(2)–O(10)	79.6(2)	O(13)–V(3)–O(14)	79.7(3)	O(17)–V(4)–O(18)	79.4(2)
V(1)–O(1)–V(2)	171.4(3)	V(2)–O(2)–V(3)	174.0(4)	V(3)–O(3)–V(4)	171.2(3)	V(4)–O(4)–V(1)	173.2(3)
V(1)–O(5)–C(1)–C(2)	2.3(9)	V(2)–O(10)–C(10)–C(9)	4.8(10)	V(4)–O(17)–C(22)–C(23)	0.2(10)		
V(1)–O(6)–C(3)–C(2)	−12.1(10)	V(3)–O(13)–C(15)–C(16)	1.1(9)	V(4)–O(18)–C(24)–C(23)	7.1(10)		
V(2)–O(9)–C(8)–C(9)	−11.7(11)	V(3)–O(14)–C(17)–C(16)	−2.7(10)				

V=O systems {*cf.* 1.59 Å in [VO(salen)] itself},[17] and comparable to the value reported for [{VO(salpn)}$_n$] [H_2salpn = *N*,*N*′-bis(salicylidene)propane-1,2-diamine] in which each V=O system is a ligand upon the next in a polymeric chain.[18] The separations [2.024(4)–2.050(5) Å] for O→V are of the order observed for H_2O→V in [$VO(H_2O)_4(SO_4)$]·H_2O (*ca.* 2.04 Å).[19] The vanadium–carbonyl oxygen atom bond distances *trans* to the V–Cl bond are shorter than those *trans* to the V=O bond while the V–Cl bond distances *trans* to vanadyl oxygen atoms and those *trans* to carbonyl oxygen atom are similar. Condensed vanadyls containing a V_4O_4 skeletal unit are known, *e.g.* $[\{VI(\eta^5\text{-}C_5H_5)\}_2\{V(\eta^5\text{-}C_5H_5)(NO)\}_2O_4]$[20] and $[\{V(\eta^5\text{-}C_5Me_5)OCl\}_4]$[21] but both are based on a four-co-ordinate (tetrahedral) metal geometry. The structure of **3** is the first example of a V_4O_4 core moiety with vanadyl oxygen bridging between six-co-ordinate metal centres. The recently reported[22] tetrameric titanoxane $[\{TiCl_2(MeCN)_2(\mu\text{-}O)\}_4]\cdot 2MeCN$ has a similar Ti_4O_4 core unit to V_4O_4 in **3**.

Polymerization Studies.—The ethylene polymerization catalysts were prepared by milling a *n*-hexane slurry of $[MgCl_2(thf)_2]$ with compounds listed in Table 3 with triethylaluminium as the cocatalyst and dichloromethane as the promoter. The results of ethylene polymerization obtained with monomeric $[VCl_3(thf)_3]$ and dimeric $[V_2(\mu\text{-}Cl)_2Cl_4(thf)_4]$ compounds are similar with *ca.* 236 kg polyethylene obtained per g V h^{-1}. This suggests that during the catalyst formation process conversion of mono- to di-meric vanadium species occurs [equation (4)].[6]

$$2[VCl_3(thf)_3] \xrightarrow{CH_2Cl_2} [V_2(\mu\text{-}Cl)_2Cl_4(thf)_4] + 2thf \quad (4)$$

Therefore the use of dichloromethane as a promoter for vanadium catalysts is necessary for di- or poly-metallic active centre formation. Hence, it follows that the propagation constant for ethylene polymerization on a bimetallic centre is probably much larger than on a mononuclear vanadium centre. The data in Table 3 demonstrate the very high activities attainable with vanadium catalysts and compare well with other high-activity vanadium catalysts.[23] Addition of $[MgCl_2(thf)_2]$ to the vanadium catalyst precursor did not significantly raise the activity, and therefore was a non-essential component. However, when the vanadium catalysts were used without $[MgCl_2(thf)_2]$ polyethylene usually fouled the reactor so badly that results were difficult to reproduce.[4] Addition of stronger chelating ligands than organic diesters to the vanadium catalyst *e.g.* 1,2-dimethoxybenzene (veratrole) led to almost total deactivation of the catalyst.[4] These results are understandable based on the structures of compounds **1** and **3**. The two carbonyl oxygen atoms of the ester molecules are *cis*-co-ordinated to each vanadium atom, and in polymerization conditions bis-vacant unsaturation active vanadium centres are formed.

Most likely veratrole co-ordinates to the vacant metal sites leading to deactivation of the catalyst. In the presence of a weaker base such as ethyl malonate or ethyl acetate the reaction between the catalyst metal site and ester is reversible. Because of low yield of compound **3**, a full polymerization test has not been carried out so far. However, preliminary results seem to show that the catalytic activity of **3** (224 kg polyethylene per g V h^{-1}) is similar to that for **1** and **2**.

Experimental

All manipulations were carried out under dinitrogen by use of standard Schlenk and vacuum line techniques. The compounds VCl_3, $AlEt_3$ and $AlEt_2Cl$ were commercial materials. Solvents were dried and purified by standard techniques. Magnetic susceptibilities were measured by the Faraday method within the temperature range 4.2–298 K. Corrections for diamagnetism were made with Pascal's constants. The EPR spectra were obtained on an SE type X-band spectrometer. UV/VIS measurements were made on Beckman UV 5240 spectrometer. Infrared spectra were obtained using a Perkin-Elmer 180 spectrometer.

Table 3 Polymerization[a] of ethylene with vanadium–$MgCl_2$–$AlEt_3$ catalysts

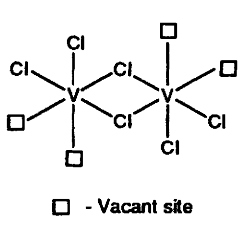
Vanadium compound	Productivity[b]/kg polyethylene per g vanadium per h
$[VCl_3(thf)_3]$	235
$[V_2(\mu\text{-}Cl)_2Cl_4(thf)_4]$	236
$[V_2(\mu\text{-}Cl)_2Cl_4(MeCO_2Et)_4]$	203
$[V_2(\mu\text{-}Cl)_2Cl_4\{CH_2(CO_2Et)_2\}_2]$	213

[a] Polymerization conditions: $[V]_o = 0.0125$ mmol dm^{-3}, Al : V = 100 : 1, Mg : V = 8 : 1, Al : promoter = 1 : 1.5, $P_{ethylene} = 0.6$ MPa, in *n*-hexane. [b] Productivity is the mass in kilograms of polymer formed per gram of vanadium atom in 1 hour.

Table 4 Crystal data and structure refinement for complexes **1** and **3**[a]

	1	**3**
Empirical formula	$C_{16}H_{32}Cl_6O_8V_2$	$C_{30}H_{52}Cl_{12}O_{20}V_4$
M	667.327	1361.875
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	8.355(7)	12.655(4)
b/Å	16.059(9)	13.735(3)
c/Å	11.323(6)	18.141(3)
α/°	90.0	86.07(2)
β/°	94.66(6)	82.14(2)
γ/°	90.0	71.74(3)
U/Å^3	2965(2)	1514(2)
D_c/g cm^{-3}	1.462(2)	1.525(1)
D_m/g cm^{-3}	1.479	1.515
μ/mm^{-1}	1.18	1.21
F(000)	680	1376
Crystal size/mm	0.5 × 0.3 × 0.3	0.5 × 0.4 × 0.4
2θ range/°	2–55	2–47
Reflections collected	3799	8801
Range *hkl*	0–8, 0–20, −14 to 14	0–13, −14 to 15, −20 to 20
Independent reflections (R_{int})	1319 (0.0232)	4786 (0.0367)
Data/parameters	1319/145	4786/605
Goodness-of-fit on F^2	1.104	1.042
Final *R* indices (all data)		
$R1$[b]	0.0407	0.0494
$wR2$[c]	0.1042	0.1353
Max. Δ/σ/Å	0.003	0.018
Max., min. electron density/e Å^{-3}	0.34, −0.23	0.65, −0.33

[a] Details in common: $T = 298(1)$ K, $Z = 2$, λ(Mo-Kα) = 0.710 71 Å. [b] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.



Synthesis.—$[V_2(\mu\text{-}Cl)_2Cl_4(MeCO_2Et)_4]$ **1**. The VCl_3 (4 g, 25.4 mmol) was placed in a Soxhlet and extracted with ethyl acetate (150 cm^3) for *ca.* 6 h until it dissolved. The solution was cooled to room temperature and left to crystallize. After 3 days red crystals were filtered off, washed with *n*-hexane (3 × 5 cm^3) and dried *in vacuo*. Yield 6.4 g (75.7%) (Found: Cl, 31.5; V, 15.1. $C_{16}H_{32}Cl_6O_8V_2$ requires Cl, 31.9; V, 15.3%). IR (Nujol mull): 310s, 356vs, 462m, 612w, 850s, 1008s, 1042vs, 1096w and 1668vs cm^{-1}. $\mu_{eff} = 2.72\ \mu_B$(4.2–293 K).

$[V_2(\mu\text{-}Cl)_2Cl_4\{CH_2(CO_2Et)_2\}_2]$ **2**. Complex **1** (1.4 g, 2.1 mmol) was dissolved in toluene–CH_2Cl_2 (40 cm^3, 1 : 1) and $CH_2(CO_2Et)_2$ (0.85 cm^3, 0.89 g, 5.5 mmol) was added by syringe and the solution stirred at room temperature for 2 h. The brown-orange solid which precipitated after addition of *n*-hexane (10 cm^3) was filtered off and washed with *n*-hexane (3 × 10 cm^3) and dried *in vacuo*. Yield 0.69 g (52%) (Found: Cl, 33.1; V, 16.0. $C_{14}H_{24}Cl_6O_8V_2$ requires Cl, 33.5; V, 16.0%). IR (Nujol mull): 300 (sh), 346s, 390m, 464m, 768w, 856m, 950m, 964w, 984m, 1022s, 1622s and 1672vs cm^{-1}, μ_{eff} = 2.42 μ_B(4.2–293 K).

Rearrangement of **2** *into* $[\{VOCl_2[CH_2(CO_2Et)_2]\}_4]\cdot 2CH_2Cl_2$ **3**.—The volume of the filtrate (obtained after separation of brown-orange complex **2**) was reduced to *ca.* 20 cm^3 and left to crystallize at 273 K. After a week the colour changed from brown to deep red and a small amount of deep red crystals of **3** and brown powder (**2**) were deposited. The crystallization process of **3** could be accelerated by passing dioxygen over the solution into the vessel while under N_2 only compound **2** precipitated. A crystal of **3** was separated by hand for the X-ray diffraction study. IR (Nujol mull): 341s, 364vs, 402s, 454m, 858s, 930s, 950m, 984w, 1024m and 1644vs cm^{-1}.

Polymerization Test.—A slurry of $[MgCl_2(thf)_2]$ (30 mmol) in *n*-hexane was milled under argon in a glass mill (capacity 250 cm^3, with 20 balls of diameter 5–15 mm) at room temperature for 6 h. Then vanadium compound (3 mmol) and *n*-hexane (50 cm^3) were added and the mixture was milled for 24 h. The sample of precatalyst suspension (containing 0.01% vanadium) was activated with $AlEt_3$ (20 mmol) for 15 min at 323 K under argon and treated with CH_2Cl_2 (30 mmol) to form the highly active catalyst. The polymerization of ethylene was carried out at 323 K in a stainless-steel reactor (1 dm^3) equipped with a stirrer, in *n*-hexane at an ethylene pressure 0.6 MPa. The polymerization was quenched with a 5% solution of HCl in methanol (150 cm^3) and the polymer was filtered off, washed with methanol and dried under vacuum.

X-Ray Crystallography.—*Data collections and processing*. Crystal data and experimental details of the samples are given in Table 4. Intensities were collected using a Kuma KM4 four-circle diffractometer in the ω–2θ mode (with crystals of dimensions 0.5 × 0.3 × 0.3 mm for **1** and 0.5 × 0.4 × 0.4 mm for **3**) and Mo-Kα radiation. The crystals were cut from large crystals and sealed in glass capillaries. For both crystals the intensities of three standard reflections, monitored every 100 intensity scans showed no evidence of crystal decay. 3799 (4 < 2θ < 55°, 3337 independent) and 8801 (4 < 2θ < 47°, 8747 independent) reflections were measured for **1** and **3**, respectively, from which 1319 and 4786 independent reflections

Table 5 Final atomic coordinates for non-hydrogen atoms of complex **1**

Atom	*x*	*y*	*z*
V	0.034 97(13)	0.485 10(6)	0.157 08(8)
Cl(1)	0.131 4(2)	0.427 70(9)	−0.023 70(12)
Cl(2)	0.242 0(2)	0.576 83(11)	0.171 6(2)
Cl(3)	−0.082 3(2)	0.528 39(12)	0.320 16(14)
O(1)	−0.123 3(5)	0.388 8(3)	0.133 5(3)
O(2)	−0.303 0(5)	0.293 3(3)	0.082 2(5)
O(3)	0.165 4(5)	0.393 9(3)	0.248 3(4)
O(4)	0.318 4(7)	0.309 5(3)	0.358 5(5)
C(1)	−0.263 5(9)	0.368 7(4)	0.116 0(6)
C(2)	−0.402 1(9)	0.422 8(5)	0.132 1(8)
C(3)	−0.171 5(11)	0.233 7(5)	0.060 5(10)
C(4)	−0.219 4(16)	0.183 6(7)	−0.035 8(11)
C(5)	0.258 6(8)	0.383 1(4)	0.335 4(6)
C(6)	0.315 1(11)	0.448 3(5)	0.420 3(6)
C(7)	0.270 3(12)	0.240 4(5)	0.274 8(12)
C(8)	0.393 6(15)	0.193 7(10)	0.256 5(16)

Table 6 Final atomic coordinates for non-hydrogen atoms of complex **3**

Atom	*x*	*y*	*z*
V(1)	0.072 07(9)	0.193 85(9)	0.370 75(6)
V(2)	0.326 97(9)	0.269 13(9)	0.326 18(6)
V(3)	0.289 48(9)	0.292 01(9)	0.127 95(6)
V(4)	0.069 32(10)	0.169 66(9)	0.171 84(6)
Cl(1)	0.053 5(2)	0.174 6(2)	0.498 54(11)
Cl(2)	−0.048 8(2)	0.358 99(15)	0.371 98(12)
Cl(3)	0.473 4(2)	0.335 7(2)	0.327 33(12)
Cl(4)	0.440 6(2)	0.101 54(15)	0.325 40(12)
Cl(5)	0.310 6(2)	0.301 1(2)	−0.000 60(11)
Cl(6)	0.170 5(2)	0.456 59(14)	0.138 83(13)
Cl(7)	−0.086 3(2)	0.115 4(2)	0.174 41(13)
Cl(8)	0.194 9(2)	0.008 0(2)	0.164 54(12)
Cl(9)*	0.229 6(3)	0.675 6(3)	0.099 6(2)
Cl(9′)*	0.397 9(2)	0.770 0(3)	0.040 80(15)
Cl(10)	0.180 7(2)	0.835 2(2)	−0.011 94(15)
Cl(11)	0.356 2(4)	0.459 8(4)	0.627 9(3)
Cl(12)	0.351 8(4)	0.537 0(6)	0.481 2(3)
O(1)	0.189 3(4)	0.220 6(4)	0.356 6(2)
O(2)	0.310 7(4)	0.286 1(4)	0.238 3(2)
O(3)	0.197 3(4)	0.230 7(3)	0.142 0(2)
O(4)	0.062 4(4)	0.185 9(3)	0.261 0(2)
O(5)	−0.073 3(4)	0.140 3(4)	0.374 0(3)
O(6)	0.151 6(4)	0.036 7(4)	0.364 7(3)
O(7)	−0.181 3(5)	0.044 6(5)	0.357 0(3)
O(8)	0.197 5(5)	−0.126 7(4)	0.336 7(3)
O(9)	0.319 2(4)	0.259 0(4)	0.446 7(3)
O(10)	0.219 0(4)	0.413 3(4)	0.353 4(3)
O(11)	0.250 5(5)	0.276 2(5)	0.565 7(3)
O(12)	0.090 3(6)	0.544 0(5)	0.408 7(4)
O(13)	0.428 7(4)	0.354 0(4)	0.121 9(3)
O(14)	0.423 3(4)	0.157 5(4)	0.120 8(3)
O(15)	0.600 1(5)	0.365 7(5)	0.128 8(3)
O(16)	0.588 5(5)	0.039 3(5)	0.127 9(4)
O(17)	0.077 5(4)	0.173 1(4)	0.051 2(2)
O(18)	−0.031 5(4)	0.316 3(4)	0.153 3(3)
O(19)	0.063 9(4)	0.229 2(4)	−0.066 2(3)
O(20)	−0.109 0(5)	0.472 2(4)	0.109 6(3)
C(1)	−0.083 1(6)	0.057 9(6)	0.359 1(4)
C(2)	0.009 1(8)	−0.033 9(6)	0.335 7(5)
C(3)	0.124 3(7)	−0.034 9(6)	0.347 1(4)
C(4)	−0.280 4(8)	0.131 5(9)	0.372 3(7)
C(5)	−0.314 7(12)	0.143 7(13)	0.450 4(10)
C(6)	0.317 1(8)	−0.132 0(9)	0.334 0(7)
C(7)	0.382 9(14)	−0.241 6(12)	0.308 7(15)
C(8)	0.248 7(6)	0.305 8(6)	0.496 1(4)
C(9)	0.153 6(6)	0.399 9(6)	0.483 9(4)
C(10)	0.159 7(6)	0.450 5(5)	0.410 3(4)
C(11)	0.334 5(11)	0.174 6(10)	0.583 0(6)
C(12)	0.316 8(20)	0.150 3(14)	0.652 9(10)
C(13)	0.060 1(22)	0.596 9(16)	0.329 4(13)
C(14)	0.138 3(29)	0.635 1(21)	0.331 0(19)
C(15)	0.527 4(7)	0.313 6(6)	0.135 0(4)
C(16)	0.576 2(6)	0.205 6(6)	0.158 4(4)
C(17)	0.521 3(7)	0.133 8(6)	0.133 9(4)
C(18)	0.559 1(10)	0.478 5(10)	0.107 4(7)
C(19)	0.505 4(14)	0.541 4(11)	0.172 9(9)
C(20)	0.546 4(11)	−0.038 9(9)	0.105 0(10)
C(21)	0.539 8(21)	−0.104 8(18)	0.161 7(10)
C(22)	0.052 7(6)	0.242 8(6)	0.006 1(4)
C(23)	0.006 2(7)	0.354 7(6)	0.023 0(4)
C(24)	−0.045 9(6)	0.376 5(6)	0.101 9(4)
C(25)	0.114 1(8)	0.124 1(7)	−0.091 3(5)
C(26)	0.128 4(14)	0.127 0(10)	−0.173 0(6)
C(27)	−0.153 1(10)	0.501 7(8)	0.186 7(6)
C(28)	−0.196 8(18)	0.613 3(10)	0.188 1(7)
C(29)	0.252 6(7)	0.789 5(8)	0.066 3(6)
C(30)	0.343 5(10)	0.564 1(10)	0.573 4(8)

* The occupancy factors for Cl(9) and Cl(9′) are 0.443(6) and 0.557(6), respectively.

with $I > 3.0\sigma(I)$ were used for calculations. The structures were solved by the Patterson method and refined by full-matrix least-squares calculations using SHELXL 93.[24] The number of refined parameters was 145 for **1** and 605 for **3**. Neutral atom scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 25; real and imaginary components of anomalous dispersion were included for all non-H atoms. The hydrogen atoms were put in calculated positions with d(C–H) = 1.08 Å and introduced as fixed contributors in the final stage of refinement. One of the CH_2Cl_2 molecules in **3** was partially disordered. Absorption corrections following the DIFABS[26] procedure were applied: minimum and maximum absorption corrections were 0.862 and 1.039 for **1** and 0.941 and 1.037 for **3**. A weighting scheme of the form $w = 1/\sigma^2(F_o^2) + (0.0517P)^2 + 2.00P$ and $w = 1/\sigma^2(F_o^2) + (0.0780P)^2 + 7.51P$ [where P is defined as $(F_o^2 + 2F_c^2)/3$] was applied for **1** and **3**, respectively. Final $R1(F)$ and $wR2(F^2)$ values are 0.0407 and 0.1042 for **1** and 0.0494 and 0.1353 for complex **3**. For the last cycle of the refinement the maximum value of the ratio Δ/σ was 0.003 and 0.018 Å for **1** and **3**, respectively. The final difference map showed a general background within −0.23 and 0.34 for **1** and −0.33 and 0.65 e Å^{-3} for **3**. Final positional parameters for complexes **1** and **3** are given in Tables 5 and 6.

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

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