2-Tetrahydrofurfuroxo-vanadium-(III) and -(IV) complexes. Synthesis, structures and reactivities of $[V_2Mg_2(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_4]\cdot 2CH_2Cl_2$ and $[V_2(\mu,\eta^2\text{-thffo})_2Cl_2O_2]$ †

Zofia Janas,[a] **Piotr Sobota,***[,a] **Maria Klimowicz,**[a] **Sławomir Szafert,**[a] **Krzysztof Szczegot**[b] **and Lucjan B. Jerzykiewicz**[a]

[a] *Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland*
[b] *University of Opole, 48 Oleska, 45-342 Opole, Poland*

Vanadium complexes of 2-tetrahydrofurfuroxide (2-tetrahydrofurylmethoxide) (thffo) with the metal in oxidation state III and IV have been prepared and characterized. The reaction of $[VCl_3(thf)_3]$ with 1.5 equivalents of $[Mg(thffo)_2]$ in tetrahydrofuran (thf) or CH_2Cl_2 led to the formation of $[V_2Mg_2(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_4]\cdot 2CH_2Cl_2$ **1**. Its structure consists of centrosymmetric tetranuclear molecules and CH_2Cl_2 of crystallization. Two Mg and two V atoms have distorted octahedral geometry and form a nearly regular Mg_2V_2 rhombus. The V · · · V distance is 3.266(2) Å. The reaction of $[VOCl_2(thf)_2]$ with Na(thffo) in thf yielded $[V_2(\mu,\eta^2\text{-thffo})_2Cl_2O_2]$ **2**. Two VOCl units are linked by alkoxide oxygen bridges. The V · · · V distance is 3.070(1) Å. Compounds **1** and **2** are very effective procatalysts for the polymerization of ethylene.

Alkoxides $M(OR)_n$ [1,2] appear as versatile potential candidates for both sol–gel [3] and metal-organic chemical vapour (MOCV) [4,5] conversion of the precursor for the final material. They are also of interest for applications in catalysis as well as in material science. Heterometallic alkoxide derivatives have been postulated to act as catalysts in Ziegler–Natta polymerization [6] or olefin-metathesis [7] reactions and also in dinitrogen activation [8] but detailed characterization is lacking. Our interest was primarily concerned with the synthesis and structural characterization of vanadium-(III) and -(IV) compounds with a 2-tetrahydrofurfuroxo (2-tetrahydrofurylmethoxo) ligand (thffo). Oxygen-containing ligands such as ether-alcohols were able to modify the vanadium active centres and produce polyethylenes with a more narrow molecular weight distribution.[9]

Previously, we have reported [10] briefly the reaction of $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) with $[Mg(thffo)_2]$ which gives the tetranuclear complex $[V_2Mg_2(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_4]$ and here we describe the structure and reactions of this compound in detail, together with the preparation, structural study and catalytic activity of the complex $[V_2(\mu,\eta^2\text{-thffo})_2Cl_2O_2]$.

Table 1 Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Mg–O(11)	2.074(4)	Mg–O(21′)	2.103(4)
Mg–O(31)	2.097(4)	Mg–O(37)	2.022(4)
Mg–O(27′)	2.007(4)	Mg–O(17)	2.171(4)
V–Cl(1)	2.391(2)	V–Cl(2)	2.385(2)
V–O(17)	2.073(4)	V–O(17′)	2.094(3)
V–O(27)	1.926(4)	V–O(37)	1.936(4)
V · · · V	3.266(2)	V · · · Mg	3.130(2)
V · · · Mg′	3.144(2)		
O(27)–V–O(37)	171.0(2)	O(27)–V–O(17)	92.6(2)
O(37)–V–O(17)	82.4(2)	O(27)–V–O(17′)	81.3(2)
O(37)–V–O(17′)	90.2(2)	O(17)–V–O(17′)	76.8(2)
O(27)–V–Cl(2)	93.4(2)	O(37)–V–Cl(2)	94.5(2)
O(17)–V–Cl(2)	94.4(2)	O(17′)–V–Cl(2)	169.4(2)
O(27)–V–Cl(1)	91.9(2)	O(37)–V–Cl(1)	92.2(2)
O(17)–V–Cl(1)	171.6(2)	O(17′)–V–Cl(1)	96.9(2)
Cl(2)–V–Cl(1)	92.4(1)	O(27′)–Mg–O(37)	95.2(2)
O(27′)–Mg–O(11)	116.8(2)	O(37)–Mg–O(11)	132.6(2)
O(27′)–Mg–O(31)	146.8(2)	O(37)–Mg–O(31)	77.5(2)
O(11)–Mg–O(31)	90.2(2)	O(27′)–Mg–O(21′)	77.4(2)
O(37)–Mg–O(21′)	130.6(2)	O(11)–Mg–O(21′)	91.9(2)
O(31)–Mg–O(21′)	83.1(2)	O(27′)–Mg–O(17)	77.6(2)
O(37)–Mg–O(17)	77.9(2)	O(11)–Mg–O(17)	76.2(2)
O(31)–Mg–O(17)	130.5(2)	O(21′)–Mg–O(17)	143.4(2)

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

Results and Discussion

Synthesis and structure of $[V_2Mg_2(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_4]\cdot 2CH_2Cl_2$ 1

Reaction of $[VCl_3(thf)_3]$ with 1.5 equivalents of $[Mg(thffo)_2]$ in thf gives a light violet microcrystalline solid which after recrystallization from CH_2Cl_2–thf (1 : 1) gave deep violet cubic-shaped crystals of $[V_2Mg_2(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_4]\cdot 2CH_2Cl_2$ **1**, equation (1). In the IR spectrum of **1** two bands at

$$2[VCl_3(thf)_3] + 3[Mg(thffo)_2] \longrightarrow \underset{\mathbf{1}}{[V_2Mg_2(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_4]} + [MgCl_2(thf)_2] \quad (1)$$

366 and 414 cm^{-1} are indicative of the terminal chloride atoms co-ordinated to vanadium in *cis* position and a band at 304 cm^{-1} is assigned to a Mg–O (ether) stretching mode of a co-ordinated thffo ligand. The temperature independent (80–293 K) magnetic moment (μ_{eff} = 2.89 μ_B) per vanadium atom is consistent with non-interacting d^2 centres. The compound is soluble in chlorinated hydrocarbons but insoluble in thf and hydrocarbons.

A crystal structure determination of compound **1** showed it to be composed of centrosymmetric tetranuclear molecules and CH_2Cl_2 of crystallization (Fig. 1). Two magnesium and two vanadium atoms form a nearly regular Mg_2V_2 rhombus with a Mg–V–Mg bond angle of 117.3(4)° and V · · · Mg distances of 3.130(2) and 3.144(2) Å, respectively (Table 1). These four metal centres are bridged by two μ_3-alkoxo oxygen atoms O(17) and O(17′) of thffo ligands, one above and one below the Mg_2V_2 plane. In addition Mg–V edges are linked by four μ-alkoxo

---

† *Non-SI units employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

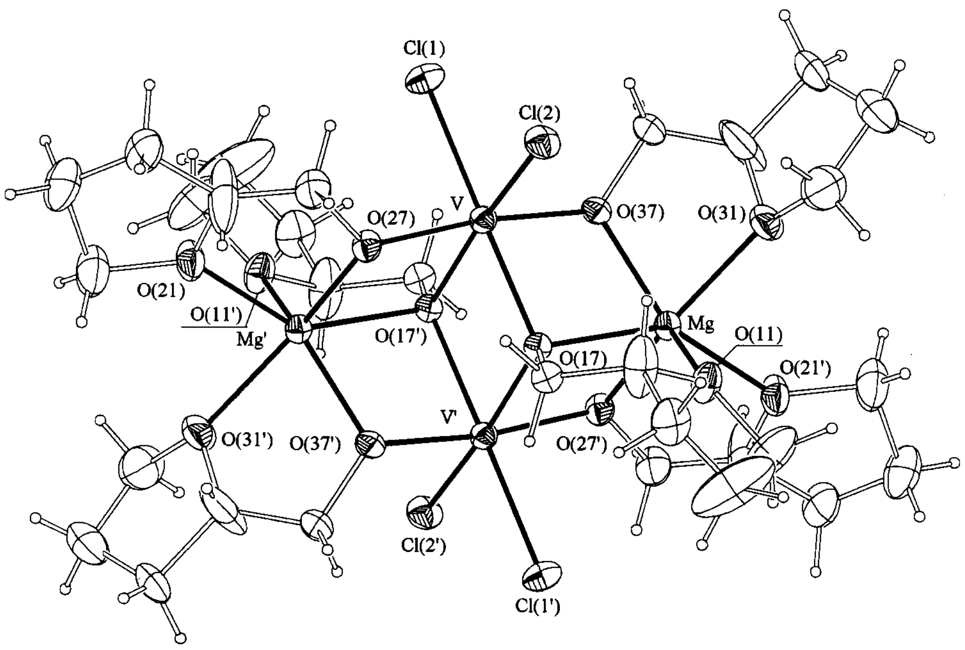

Fig. 1 Molecular structure of compound **1** with the atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. Primed atoms are related to unprimed ones by $-x, 1 - y, 1 - z$

oxygen atoms and all the metal centres show distorted octahedral geometry. The major distortions from idealized octahedral geometry around magnesium atoms are for the O(27′)–Mg–O(31), O(37)–Mg–O(31) and O(37)–Mg–O(21′) angles, with values of 146.8(2), 77.5(2) and 130.6(2)°, respectively. For the vanadium atoms distortion is less extreme [O(17)–V–O(17′) 76.8(2) and O(17′)–V–Cl(2) 169.4(2)°]. The co-ordination sphere of the magnesium atoms is formed only by ether and alkoxo oxygen atoms of the 2-tetrahydrofurfuroxo ligands whereas each vanadium atom is co-ordinated by alkoxo oxygen atoms and additionally by two terminal chlorides. The V···V distance of 3.266(2) Å is well outside the metal–metal bonding range but is distinctly shorter than that found in the vanadium(III) dimer $[V_2(\mu\text{-Cl})_2Cl_4(thf)_4]$ [3.619(1) Å].[11] The V–Cl bond lengths of 2.391(2) and 2.385(2) Å are significantly longer than those observed in $[VCl_3(thf)_3]$ [2.297(2) and 2.330(3) Å][12] or $[V_2(\mu\text{-Cl})_2Cl_4(thf)_4]$ [2.300(1) and 2.292(1) Å].[11] The average Mg–O (ether) and Mg–μ-O (alkoxo) distances of 2.092(4) and 2.014(4) Å, respectively, are generally similar to the corresponding bond lengths found in $[Mg_4(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_2]$.[13] However, the Mg–$\mu_3$-O(17) distance of 2.171(4) Å is longer than for Mg–μ_3-O found in $[Mg_4(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_2]$ [average 2.066(3) Å].[13]

Synthesis and structure of $[V_2(\mu,\eta^2\text{-thffo})_2Cl_2O_2]$ 2

The reaction of $[VCl_3(thf)_3]$ with Na(thffo) in 1:1 molar ratio in thf gave a poorly defined olive product from which during recrystallization (thf–hexane) dark blue crystals of $[V_2(\mu,\eta^2\text{-thffo})_2Cl_2O_2]$ **2** were isolated in very low yield (*ca.* 10%). Higher yields (*ca.* 80%) could be obtained from a direct reaction of $[VOCl_2(thf)_2]$ with Na(thffo) in thf, equation (2). Compound **2**

$$2[VOCl_2(thf)_2] + 2Na(thffo) \xrightarrow{thf} \underset{\mathbf{2}}{[V_2(\mu,\eta^2\text{-thffo})_2Cl_2O_2]} + 2NaCl \quad (2)$$

has low solubility in thf and CH_2Cl_2 and is insoluble in hydrocarbons.

The IR spectrum of compound **2** contains absorptions due to V–Cl stretching vibrations at 380 and 360 cm^{-1}. The region between 930 and 1050 cm^{-1}, where generally the V=O stretch appears, is crowded due to absorption from the thffo ligand making identification of ν(V=O) impossible. The EPR spectrum in thf at room temperature consists of eight principal lines (^{51}V, $I = \frac{7}{2}$) and is typical for a mononuclear VO^{2+} species. It could suggest that the dinuclear structure in the solid state is not retained in solution or the metal centres are negligibly interacting. The isotropic parameters g_{iso} and A_{iso} are 1.9853 and 111 G, respectively. The solid-state EPR spectrum of **2** shows only a single broad line (ΔH = 143 G, g = 1.981). This suggests very weak interaction of the metallic centres. The solid-state magnetic moment of μ_{eff} = 1.56 μ_B per vanadium suggested weak antiferromagnetic coupling between the vanadium(IV) atoms. Although we have not done a complete temperature-dependent magnetic study and hence cannot determine the exchange-coupling constant, $-2J$, the magnitude of the room-temperature moment indicates that the degree of exchange coupling in **2** is similar to that in $[\{VO(salahe)\}_2]$ [H_2salahe = 2-(salicylideneamino)ethanol][14] and phenoxo-bridged complexes reported by Ginsberg.[15]

Table 2 Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for complex **2**

V(1)–Cl(1)	2.292(2)	V(2)–Cl(2)	2.283(2)
V(1)–O(1)	1.576(5)	V(2)–O(2)	1.587(4)
V(1)–O(17)	1.967(4)	V(2)–O(17)	1.951(4)
V(1)–O(11)	2.001(4)	V(2)–O(27)	1.956(4)
V(1)–O(27)	1.958(5)	V(2)–O(21)	2.025(4)
V(1)···V(2)	3.070(1)		
Cl(1)–V(1)–O(1)	106.9(2)	Cl(2)–V(2)–O(2)	109.6(2)
Cl(1)–V(1)–O(17)	143.8(2)	Cl(2)–V(2)–O(17)	94.2(2)
Cl(1)–V(1)–O(11)	91.8(2)	Cl(2)–V(2)–O(27)	138.8(2)
Cl(1)–V(1)–O(27)	93.4(2)	Cl(2)–V(2)–O(21)	90.5(2)
O(1)–V(1)–O(17)	109.3(3)	O(2)–V(2)–O(17)	107.0(3)
O(1)–V(1)–O(11)	106.6(3)	O(2)–V(2)–O(27)	111.5(3)
O(1)–V(1)–O(27)	107.9(3)	O(2)–V(2)–O(21)	104.3(3)
O(17)–V(1)–O(11)	77.5(2)	O(17)–V(2)–O(27)	76.6(2)
O(17)–V(1)–O(27)	76.2(2)	O(17)–V(2)–O(21)	144.6(2)
O(11)–V(1)–O(27)	141.9(2)	O(27)–V(2)–O(21)	76.9(2)

A dimeric formulation for compound **2** was confirmed by X-ray crystallography, which showed two VOCl units linked by alkoxide oxygen bridges as illustrated in Fig. 2. Bond lengths and angles are listed in Table 2. The strain involved in co-ordinating the alkoxide oxygens O(17) and O(27) leads to a highly distorted polyhedron in which the four-atom $[V(OR)]_2$

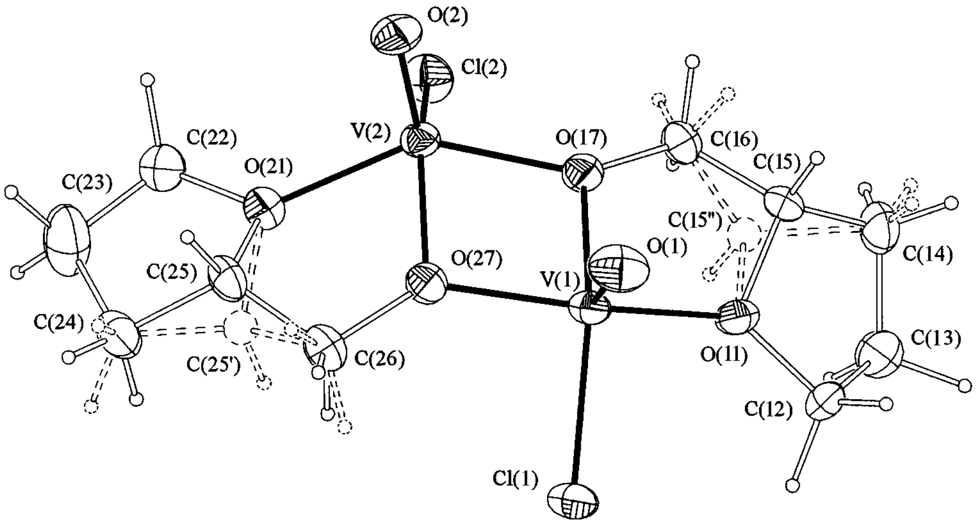

Fig. 2 Molecular structure of compound **2** with the atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. The second position of the disordered atoms is denoted by dashed lines

Table 3 Polymerization[a] of ethylene with vanadium–$MgCl_2$–$AlEt_2Cl$ catalysts

T/K	Productivity[b] /kg per gV per h	
	1	**2**
303	39	36
323	495	263
343	510	397

[a] Conditions: $[V]_0 = 0.01$ mmol dm^{-3}, [Al] = 5 mmol dm^{-3}; Mg : V = 10 : 1; $P_{ethylene} = 0.6$ MPa; in hexene. [b] The mass in kilograms of polymer formed per gram of vanadium atom in 1 h.

core is bent and the two vanadyl groups are in a '*syn*' configuration. The V–O (alkoxide) distances, which average 1.958(4) Å, are similar to those found in [{VO(salahe)}$_2$] [average 1.983(10) Å][14] and $Na_2[\{V(O)L\}_2]\cdot CH_3OH\cdot 3H_2O$ (L = 3-hydroxy-3-methylglutarate) [average 1.976(8) Å].[16] The V–Cl and V=O distances, average 2.288(2) and 1.581(5) Å respectively, are typical of those in chlorovanadyl(IV) complexes.[17,18] The V···V distance of 3.070(1) Å is well comparable to that recorded for [{VO(salahe)}$_2$] [3.068(4) Å].[14] To our knowledge compound **2** represents the first structurally characterized alkoxo-bridged vanadyl(IV) centres with an ether alkoxide ligand. Hitherto, structurally characterized examples of dimeric vanadium(IV) complexes containing a $[OV(\mu\text{-}OR)_2VO]^{2+}$ core have only been reported for [{VO(salahe)}$_2$],[14] $Na_2[\{V(O)L\}_2]\cdot CH_3OH\cdot 3H_2O$[16] and six-co-ordinate vanadyl(IV) with a Schiff base.[19]

Polymerization studies

The ethylene polymerization catalysts were prepared by milling a *n*-hexane slurry of $[MgCl_2(thf)_2]$ with the vanadium compound and chlorodiethylaluminium as the cocatalyst. The results of ethylene polymerization are shown in Table 3. The catalytic activity of both systems increases with temperature and is the highest at 343 K, yielding 510 and 397 kg polyethylene (g V $h^{-1})^{-1}$ (Mg : V = 16 : 1, $[V]_0 = 0.005$ mmol dm^{-3} and [Al] = 5 mmol dm^{-3}) for **1** and **2** respectively. For comparison, under the same conditions, the best results for catalysts based on $[VCl_3(thf)_3]$ and $[VCl(C_6H_3Pr^i_2)_2(thf)_2]$ were 235 and 243 kg polyethylene (g V $h^{-1})^{-1}$ respectively.[18,20] The catalysts based on **1** and **2** are particularly stable during the polymerization reaction. The highest activities were obtained after 2–3 min and did not decrease in time even by 30 min, that is there was no maximum in the relationship between activity and time of the polymerization reaction. Addition of $[MgCl_2(thf)_2]$ to the vanadium catalyst precursors did not significantly raise the activity and therefore was a non-essential component. However the use of vanadium catalysts without $[MgCl_2(thf)_2]$ fouls the reactor by polymer so badly that the results are difficult to reproduce. Note that vanadium catalysts are very important in ethylene–propylene rubber production.[21]

Conclusion

We have demonstrated the synthesis, crystal structures and reactivity of $[V_2Mg_2(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_4]$ **1** and $[V_2(\mu,\eta^2\text{-thffo})_2Cl_2O_2]$ **2**. Both **1** and **2** show extremely high catalytic activity in ethylene polymerization compared to vanadium chloride-based catalysts. Complexes **1** and **2** represent the first examples of tetranuclear heterometallic V–Mg and dimeric ether–alkoxo compounds, respectively. The knowledge of their molecular structures is of great importance not only for the polymerization process but also may be of relevance for better understanding of the mechanisms of biocatalysts. Compound **1** may be considered to model vanadium nitrogenase[22] and **2** vanadate-dependent haloperoxidases.[23]

Experimental

All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. All the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The compounds $[VCl_3(thf)_3]$,[24] $[VOCl_2(thf)_2]$[25] and $[Mg(thffo)_2]$[13] were prepared by literature methods. 2-Tetrahydrofurfuryl alcohol was obtained from the Aldrich Chemical Co. and distilled under vacuum before use. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer in Nujol mulls, EPR spectra on a Bruker ESP 300E spectrometer. Magnetic moment determinations in the solid state used a Faraday balance.

Preparations

$[V_2Mg_2(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_4]\cdot 2CH_2Cl_2$ 1. To $[VCl_3(thf)_3]$ (0.48 g, 1.28 mmol) dissolved in thf (20 cm^3) was added $[Mg(thffo)_2]$ (0.44 g, 1.94 mmol). After stirring overnight, the light violet solid was filtered off, washed with thf (3 × 5 cm^3) and dried under vacuum. Analytically pure deep violet large cubic-shaped crystals of compound **1** were obtained by slow diffusion of thf into a solution of the crude product in CH_2Cl_2. Yield 0.54 g (80%) (Found: C, 35.4; H, 5.3; Cl, 13.0; Mg, 4.4. $C_{32}H_{58}Cl_8Mg_2O_{12}V_2$ requires C, 36.0; H, 5.5; Cl, 13.3; Mg, 4.5%). IR (Nujol mull): 1275w, 1255w, 1190w, 1054s, 1006w, 984w, 940w, 812s, 626m, 590w, 486s, 444s, 414m, 366m and 304s cm^{-1}. μ_{eff} = 2.89 μ_B (79–299 K).

Table 4 Crystal and structure refinement data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{32}H_{58}Cl_8Mg_2O_{12}V_2$	$C_{10}H_{18}Cl_2O_6V_2$
M	1068.88	407.03
T/K	294(2)	298(1)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	9.942(2)	9.356(3)
b/Å	15.702(3)	9.197(4)
c/Å	15.449(3)	18.696(7)
β/°	98.26(3)	96.22(3)
U/Å^3	2386.7(8)	1599(2)
Z	2	4
D_c/g cm^{-3}	1.487	1.690
μ/mm^{-1}	0.917	1.52
F(000)	1104	824
θ Range/°	2–23	2–23
h,k,l Ranges	0–10, 0–17, −16 to 16	0–10, 0–10, −22 to 22
Reflections collected	2598	2990
Independent reflections	2444	1276
Parameters	280	191
Goodness to fit on F^2	1.079	1.088
Final $R1$ [$I > 2\sigma(I)$]	0.0510	0.0383
$wR2$ [$I > 2\sigma(I)$]	0.1398	0.0964

$R1 = \Sigma(F_o - F_c)/\Sigma F_o$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

$[V_2(\mu,\eta^2\text{-thffo})_2Cl_2O_2]$ 2. *Method* 1. A thf solution of [Na(thffo)] [prepared *in situ* by treating tetrahydrofurfuryl alcohol (0.5 cm^3, 5.16 mmol) with NaH (0.12 g, 5.16 mmol) in thf (50 cm^3)] was treated with $[VCl_3(thf)_3]$ (0.7 g, 1.87 mmol). The resulting mixture changed from pink to brown-green and was stirred at room temperature overnight. After filtration and concentration, hexane was added to yield an olive solid. This was recrystallized from thf–hexane (1 : 1). Dark blue crystals suitable for structure determination were obtained upon standing for 3 d at room temperature. Yield: 0.04 g (10%).

Method 2. A solution of tetrahydrofurfuryl alcohol (0.46 cm^3, 4.74 mmol) in thf (30 cm^3) was stirred overnight with NaH (0.11 g, 4.6 mmol). On addition of $[VOCl_2(thf)_2]$ (1.35 g, 4.8 mmol) the mixture turned dark blue. It was stirred for 12 h and filtered, then the solvent was removed *in vacuo*. The solid residue was redissolved in CH_2Cl_2, filtered off from NaCl and the filtrate concentrated to yield a light blue solid. Yield 0.78 g (80%). Primarily X-ray examination of the crystals showed the same cell parameters as those obtained by method 1 (Found: C, 29.3; H, 4.3; Cl, 17.2. $C_{10}H_{18}Cl_2O_6V_2$ requires C, 29.5; H, 4.4; Cl, 17.4%). IR (Nujol mull): 1298w, 1288w, 1188w, 1045s, 1004vs, 978m, 940s, 920m, 884w, 868w, 806s, 656s, 594m, 558w, 515s, 450m, 380m, 360vs and 276m cm^{-1}. μ_{eff} = 1.56 μ_B (79–299 K).

Polymerization test

A slurry of $MgCl_2$ (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 the vanadium compound (3 mmol) and *n*-hexane (50 cm^3) were added and the mixture was milled for 24 h. The sample of procatalyst suspension (containing 0.01% vanadium) was activated with $AlEt_3$ (20 mmol) for 15 min at 323 K under argon to form a 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 of 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.

Crystallography

Intensities were collected using a Kuma KM4 four-circle diffractometer[26] in the ω–2θ mode with crystal of dimensions 0.4 × 0.4 × 0.3 (**1**) and 0.8 × 0.5 × 0.4 (**2**) and Mo-Kα radiation (λ 0.710 69 Å). The intensities of three standard reflections, monitored every 100 intensity scans, showed no evidence of crystal decay for all crystals. For compound **1** absorption corrections following the DIFABS[27] procedure were applied: minimum and maximum 0.883 and 1.213. The structures were solved by the Patterson method (SHELXS 86)[28] and refined (based on F^2) by full-matrix least-squares calculations using SHELXL 93.[29] The carbon-bonded H atoms were included in calculated positions and refined using a riding model with isotropic displacement parameters equal to $1.2U_{eq}$ of the attached C atom. In **1** the high value of the anisotropic displacement parameters for some atoms of CH_2Cl_2 and thffo molecules indicated possible disorder. Owing to this we tried to solve the structure with these atoms occupying two or other sites. As a result two atoms of CH_2Cl_2 were found to be disordered between two and three positions, respectively. In case of thffo molecules the disorder was not solved. Similarly to other structures with thffo,[30] in **2** residual electron densities on the Fourier-difference map in the vicinity of the chiral C(15) and C(25) atoms were found. As previously this might be explained by the assumption that enantiomers of the chelating ligand occupy the same crystallographic position, so we used a model in which only the carbon atoms C(15) and C(25), attached H atoms as well as H atoms on adjacent carbon atoms of both enantiomers had different positions. The remaining atoms of ligands were assumed to overlap.[30] The refined site-occupation factors for the major components of C(15) and C(25) atoms were 0.84 and 0.65, respectively. Weighing schemes of the form $w = 1/\sigma^2(F_o^2) + (0.0831P)^2 + 5.05P$ (**1**) and $1/\sigma^2(F_o^2) + (0.0508P)^2 + 3.31P$ (**2**) [where P is defined as $(F_o^2 + 2F_c^2)/3$] were applied. The final difference map showed a general background within −0.57 and 0.71 (**1**) and −0.30 and 0.30 e Å^{-3} (**2**). The crystal data are summarized in Table 4.

CCDC reference number 186/677.

Acknowledgements

The authors thank the State Committee for Scientific Research for financial support of this work (Grants No. 3T09A 016 08 and 3T09B 038 08).

References

1 D. C. Bradley, R. C. Mahrotra and D. P. Gaur, *Metal Alkoxides*, Academic Press, London, 1978; D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259.

2 R. C. Mahrotra, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 269.

3 L. G. Hubert-Pfalzgraf, *New J. Chem.*, 1987, **11**, 663.

4 D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.

5 L. G. Hubert-Pfalzgraf, M. C. Massiani, R. Papiernik and O. J. Poncelet, *J. Phys. Colloq.*, 1989, **50**, C5.

6 M. Takeda, K. Imura, Y. Nozawa, M. Hisatone and N. Koide, *J. Polym. Sci.*, 1968, **25C**, 741.

7 H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, 1980, **18**, 99.

8 M. E. Volpin, *J. Organomet. Chem.*, 1980, **200**, 319.

9 F. J. Karol and S. C. Kao, *New J. Chem.*, 1994, **18**, 9.

10 Z. Janas, P. Sobota, M. Kasprzak and T. Głowiak, *Chem. Commun.*, 1996, 2727.

11 P. Sobota, J. Ejfler, S. Szafert, K. Szczegot and W. Sawka-Dobrowolska, *J. Chem. Soc., Dalton Trans.*, 1993, 2353.

12 F. A. Cotton, S. A. Duraj, G. L. Powell and W. J. Roth, *Inorg. Chim. Acta*, 1986, **113**, 81.

13 P. Sobota, J. Utko, Z. Janas and S. Szafert, *Chem. Commun.*, 1996, 1923.

14 C. J. Carrano, C. M. Nunn, R. Quan, J. A. Bonadies and V. L. Pecoraro, *Inorg. Chem.*, 1990, **29**, 944.

15 A. P. Ginsberg, E. Koubek and H. J. Williams, *Inorg. Chem.*, 1966, **5**, 1656.

16 S. L. Castro, M. E. Cass, F. J. Hollander and S. L. Bartley, *Inorg. Chem.*, 1995, **34**, 466.
17 P. T. Greene and P. L. Orioli, *J. Chem. Soc. A*, 1969, 1621.
18 P. Sobota, J. Ejfler, S. Szafert, T. Głowiak, I. O. Fritzky and K. Szczegot, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1727.
19 W. Plass, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 627.
20 R. A. Henderson, D. L. Hughes, Z. Janas, R. L. Richards, P. Sobota and S. Szafert, *J. Organomet. Chem.*, in the press.
21 F. K. Karol, *Macromol. Symp.*, 1995, **89**, 563.
22 R. L. Richards, *Coord. Chem. Rev.*, 1996, **154**, 83.
23 W. Priebsch and D. Rehder, *Inorg. Chem.*, 1990, **29**, 3013 and refs. therein.
24 L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 138.
25 R. J. Kern, *J. Inorg. Nucl. Chem.*, 1962, **24**, 1105.
26 *Kuma KM4 software. User's Guide*, version 6.1, Kuma Diffraction, Wrocław, 1996.
27 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
28 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.
29 G. M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, 1993.
30 Z. Olejnik, T. Lis, J. Utko and P. Sobota, *Acta Crystallogr.*, *Sect. C*, 1996, **52**, 847.

Received 2*nd June* 1997; *Paper* 7/03828C