Synthesis and molecular structure of a tetranuclear vanadium(III)–magnesium(II) complex; a procatalyst for the alkene polymerization process

Zofia Janas, Piotr Sobota,* Maria Kasprzak and Tadeusz Głowiak

Faculty of Chemistry, University of Wroclaw, 14 F. Joliot-Curie, 50-383 Wroclaw, Poland

Treatment of [$VCl_3(thf)_3$] (thf = tetrahydrofuran) with [$Mg(thffo)_2$] (thffo = 2-tetrahydrofurfuroxide) in 1 : 1.5 ratio in thf provides the tetranuclear [$V_2Mg_2(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_4$]·$2CH_2Cl_2$ complex, for which a structural study and catalytic activity in ethene polymerization process are reported.

Heterometallic V–Mg and Ti–Mg alkoxides have been reported to be formed in the course of alkylation reactions which were designed to generate catalytic species for Ziegler–Natta polymerization reactions.[1] It was found that alkene polymerization components prepared by reacting the magnesium alkoxides with titanium tetrachloride are capable of producing polymer with improved activity and also possessing excellent morphology.[2] Whereas the Ti–Mg alkoxides are well characterized, *e.g.* the hexanuclear [$Ti_4Mg_2(\mu$-$Cl)_4(\mu$-$OEt)_4(\mu_3$-$OEt)_4(OEt)_8$] complex was obtained from the reaction of $MgCl_2$ and [$Ti(OEt)_4$] in hexane,[3] to our knowledge there is no report concerning the composition and structure of V–Mg alkoxo species.

Our work was primarily concerned with synthesis and characterization of a vanadium(III)–magnesium(II) compound with the bidendate (O-donor functions) alkoxo ligand, 2-tetrahydrofurfuroxo (thffo) as a potential polymerization procatalyst. The thffo ligand seemed to have attractive features. Containing two oxygen donor atoms, ether and alkoxide it can act not only as a chelate ligand and occupy two coordination sites on the metal, *e.g.* as in [$Ti(\eta^2$-thffo)(thf)Cl_3],[4] but also as a tether between the metal atoms to create multinuclear species, *e.g.* [$Mg_4(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_2$].[5] It should be noted that derivatives with free ether functions of the thffo ligand, that is, not coordinated to the metal ('dangling ligand') are also possible, *e.g.* [Ti(tmen)(η^1-thffo)Cl_3] (tmen = $Me_2NCH_2CH_2NMe_2$).[6] The latter type of coordination is important particularly for any study on the reactivity and catalytic behaviour of alkoxo-metal complexes because the open site on the metal is potentially capable of binding small molecules.

Here we describe the preparation, structural study and catalytic activity of the complex [$V_2Mg_2(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_4$]·$2CH_2Cl_2$ **1**. Reaction of [$VCl_3(thf)_3$] with 1.5 equiv. of [$Mg(thffo)_2$] in thf gives light-violet microcrystalline solid which after recrystallization from CH_2Cl_2–thf (1 : 1) gave deep-violet cubic-shaped crystals of [$V_2Mg_2(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_4$]·$2CH_2Cl_2$ **1**. In the IR spectrum of **1**, two bands at 366 and 414 cm^{-1} are indicative of the terminal chloride atoms coordinated to vanadium in *cis* position and a band at 304 cm^{-1} is assigned to the Mg–O(ether) stretching mode of a coordinated thffo ligand. The temperature independent (80–293 K) magnetic moment (μ_{eff} = 2.89 μ_B) per vanadium atom in **1** is consistent with non-interacting d^2 centres. The compound **1** is soluble in chlorinated hydrocarbons but insoluble in thf and hydrocarbons. Preliminary results of ethene polymerization by the **1**/$MgCl_2(thf)_2/AlEt_2Cl$ cocatalyst system shows *ca.* 410 kg polyethylene (g V h^{-1}) (Mg : V = 16; $[V]_0$ = 0.005 mmol dm^{-3}, [Al] = 5 mmol dm^{-3}). For comparison, under the same conditions, the best result of a catalyst based on [$VCl_3(thf)_3$] is 235 kg polyethylene (g V h^{-1}) (ref. 7).

An X-ray crystal structure determination of **1** showed it to be composed of centrosymmetric tetranuclear molecules† and CH_2Cl_2 molecules of crystallization (Fig. 1). Two magnesium and two vanadium atoms form a nearly regular Mg_2V_2 rhombus with an Mg–V–Mg′ bond angle of 117.3(4)° and V–Mg and V–Mg′ bond lengths of 3.130(2) and 3.144(2) Å, respectively. 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 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 146.9(2), 77.5(2) and 130.5(2)°, respectively. For the vanadium atoms the distortion is less extreme [O(17)–V–O(17′) 76.8(2)° and O(17′)–V–Cl(2) 169.4(1)°]. The coordination sphere of the magnesium atoms is formed only by ether and alkoxo oxygen atoms of the 2-tetrahydrofurfuroxo ligands, whereas each vanadium atom is coordinated by alkoxo oxygen atoms and also 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 [$V_2(\mu$-$Cl)_2Cl_4(thf)_4$] [3.619(1) Å].[8] 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), 2.330(3) Å][9] and [$V_2(\mu$-$Cl)_2Cl_4(thf)_4$] [2.300(1), 2.292(1) Å].[8] The average Mg–O(ether) and Mg–μ-O)(alkoxo)

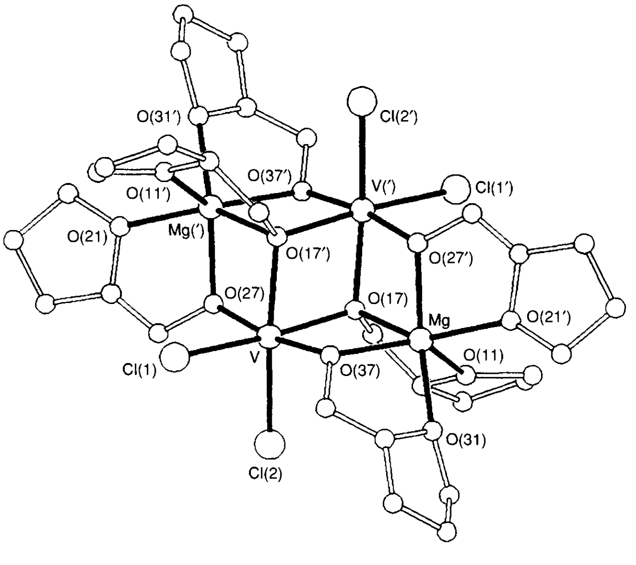

Fig. 1 The structure of [$V_2Mg_2(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_4$]·$2CH_2Cl_2$ **1** [H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): V···V 3.266(2), V···Mg 3.130(2), V···Mg′ 3.144(2), Mg–O(11) 2.074(4), Mg–O(21′) 2.103(4), Mg–O(31) 2.097(4), Mg–O(37) 2.022(4), 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(3), V–O(17′) 2.094(3), V–O(37) 1.936(4); O(27′)–Mg–O(31) 146.9(2), O(37)–Mg–O(31) 77.5(2), O(37)–Mg–O(21′) 130.5(2), O(17)–V–O(17′) 76.8(1), O(17)–V–Cl(2) 169.4(1).

distances of 2.092(4) and 2.014(4) Å, respectively, are generally similar to the corresponding bond lengths found in [$Mg_4(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_2$].[5] However, the Mg–μ_3-O(17) distance of 2.171(4) Å is longer than for Mg–μ_3-O found in [$Mg_4(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_2$] [av. 2.066(3) Å].[5]

Compound **1** is the first example of a tetranuclear heterometallic V–Mg alkoxo complexes. The knowledge of its molecular structure has great importance not only for polymerization processes but also for vanadium nitrogenase modelling studies. Since the discovery by Shilov and coworkers that a $V(OH)_2/Mg(OH)_2$ system acts as a one-electron reductant for the transformation of dinitrogen to N_2H_4 and NH_3,[10] detailed characterization of the active species formed in this system is still lacking. It is noteworthy that an Mo–Mg oxomethoxide has been structurally characterized and shown to act as a precursor of a catalyst for dinitrogen reduction.[11]

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Footnote

† *Crystal data* for **1**: $C_{32}H_{56}Cl_8Mg_2O_{12}V_2$, M = 1068.88, monoclinic, space group $P2_1/n$, a = 9.942(2), b = 15.702(3), c = 15.449(3) Å, β = 98.26(3)°, U = 2386.7(8) Å^3, Z = 2, D_c = 1.487 g cm^{-3}, μ = 9.17 cm^{-1}, $F(000)$ = 1104, T = 294(2) K, Mo-Kα radiation (λ = 0.71069 Å). Preliminary data for the crystal were obtained from Weissenberg photographs. Intensities were collected using Kuma KM4 four-circle diffractometer in the ω–2θ mode with a crystal of dimensions 0.5 × 0.5 × 0.65. Cell parameters were obtained from a least-squares fit of the setting angles of 40 reflections in the range $19.2 < 2\theta < 36.8°$. For the crystal the intensities of three standard reflections, monitored every 100 intensity scans showed no evidence of crystal decay. 2598 ($4 < 2\theta < 46°$) reflections were measured from which 2444 independent reflections with $I > 3.0\sigma(I)$ were used for calculations. The structure was solved by the Patterson method and refined by full-matrix least-squares calculations on F^2 using SHELXL93.[12] The number of refined parameters was 280. The hydrogen atoms were placed in calculated positions with d(C–H) = 0.96 Å and introduced as fixed contributors. The CH_2Cl_2 molecule was partially disordered; final R_1 = 0.0510 and wR_2 = 0.1398. A weighting scheme of the form $w = 1/\sigma^2(F_o^2) + (0.0831P)^2 + 5.05P$ was applied. For the last cycle of the refinement the maximum value of the ratio Δ/σ was below 0.005 Å. The final difference map showed a general background within −0.57 and 0.71. e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/277.

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