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Synthesis and molecular structure of vanadium(III) dithiolate complexes: a new class of alkene polymerization catalysts

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The synthesis and catalytic activity in ethylene polymerization of new vanadium complexes of 2,2′-oxydiethanethiolate $[O(CH_2CH_2S)_2{}^{2-}]$ are described; the complexes $[V(\mu\text{-}DIPP)_2\{O(CH_2CH_2S)_2\}Li(MeCN)_2]$ and $[V(DIPP)\{O(CH_2CH_2S)_2\}(py)]$ [DIPP = $(OC_6H_3Pr^i{}_2\text{-}2,6)^-$] have been structurally characterized.

The synthetic development of well defined single-site vanadium catalysts for alkene polymerization is of extremely high industrial importance[1,2] because such catalysts are able to produce high molecular weight polymers with narrow molecular weight distribution as well as α-olefin copolymers with high α-olefin incorporation.[3,4] A recent trend has been the incorporation of sulfur-containing ligands: *e.g.* $(TBP)TiCl_2$/MAO catalyst [TBP = 2,2′-thiobis(6-*tert*-butyl-4-methylphenoxide, MAO = methylaluminoxane] was ten-fold more effective in ethylene polymerization than are metallocenes catalysts.[5,6] Moreover, it is well known that vanadium-based enzyme *nitrogenase* in which vanadium is thought to be bound to sulfur-, oxygen- and nitrogen-donor ligands is able to convert acetylene into ethylene and ethane.[7] These aspects of vanadium catalysis prompted us to prepare novel vanadium compounds with thiolate ligands such as 2,2′-oxydiethanethiolate $[O(CH_2CH_2S)_2{}^{2-}]$ and study their reactions with alkenes, particularly their potential as precursors of new ethylene polymerization catalysts.

Studies of the oxidation state of active vanadium catalysts for ethylene polymerization by different investigators has led to the proposal that V^{III} and V^{II} represent the important oxidation states in the ethylene polymerization process.[8,9] Herein we report the synthesis, structural characterization and catalytic activity of the vanadium(III) heterodinuclear complexes $[V(\mu\text{-}DIPP)_2\{O(CH_2CH_2S)_2\}Li(L)_2]$ **1**, **2** and the mononuclear complex $[V(DIPP)\{O(CH_2CH_2S)_2\}(py)]$ **3** [DIPP = $(OC_6H_3\text{-}Pr^i{}_2\text{-}2,6)^-$, py = C_5H_5N; L = THF **1** or MeCN **2**].

Dark pink $[V(\mu\text{-}DIPP)_2\{O(CH_2CH_2S)_2\}Li(THF)_2]$ **1** was prepared by reaction of $[V(\mu\text{-}DIPP)_2(DIPP)_2Li(THF)]$[10] with an excess of $O(CH_2CH_2SH)_2$ in a mixture of hexane–THF [eqn. (1)].

$$[V(\mu\text{-}DIPP)_2(DIPP)_2Li(THF)] + O(CH_2CH_2SH)_2 + L \longrightarrow [V(\mu\text{-}DIPP)_2\{O(CH_2CH_2S)_2\}Li(L)_2] + 2DIPPH \qquad (1)$$

L = THF **1** or MeCN **2**

Recrystallization of **1** from MeCN gave new X-ray quality red crystals of $[V(\mu\text{-}DIPP)_2\{O(CH_2CH_2S)_2\}Li(MeCN)_2]$ **2** [eqn. (1)]. Addition of pyridine to toluene solutions of compounds **1** and **2** breaks up the heterodinuclear structures forming the monomeric species $[V(DIPP)\{O(CH_2CH_2S)_2\}(py)]$ **3** in 85% yield (eqn. (2)].

Complex **3** can be also prepared but in lower yield (53%), by reaction of $[V(DIPP)_3(py)_2]$[11] with 1 equiv. of $O(CH_2CH_2SH)_2$ in toluene. The temperature independent (80–293 K) magnetic moments of 2.6 and 2.7 μ_B per vanadium atom in **2** and **3** respectively, are consistent with non-interacting d^2 centres.

$$[V(\mu\text{-}DIPP)_2\{O(CH_2CH_2S)_2\}Li(THF)_2] + py \longrightarrow [V\{O(CH_2CH_2S)_2\}(DIPP)_3(py)] + Li(DIPP) + 2THF \qquad (2)$$

3

The crystal structure of the heterodinuclear complex **2** is shown in Fig. 1.† Complex **2** contains a five-coordinate V^{III} center adopting a slightly distorted trigonal bipyramidal geometry. Two sulfur atoms from the $O(CH_2CH_2S)_2{}^{2-}$ ligand and an aryloxide oxygen O(21) of DIPP occupy the equatorial positions. The second aryloxide oxygen O(11) and the ether oxygen O(1) from the $O(CH_2CH_2S)_2{}^{2-}$ group fill the axial sites. Both aryloxide oxygen atoms are engaged in the bridging interaction to Li, inducing distortion from the ideal trigonal bipyramidal geometry. A similar double-bridged $V(\mu\text{-}DIPP)_2Li$ unit is present in the starting material $[V(\mu\text{-}DIPP)_2(DIPP)_2\text{-}Li(THF)]$. The average V–S(thiolate) distance in **2** is 2.290(4) Å, within the range expected for V–S single bonds and comparable to other vanadium(III) thiolato complexes.[12–15]

The X-ray analysis of **3** reveals a mononuclear complex $[V(DIPP)\{O(CH_2CH_2S)_2\}(py)]$ with slightly distorted trigonal-bipyramidal coordination around the vanadium centre (Fig. 2).† The V–S and V–O(aryloxide) bond distances in the equatorial plane [V–S 2.2970(9), 2.2987(8) Å; V–O 1.8619(13) Å] do not differ significantly from those found in complex **2**. The V–N

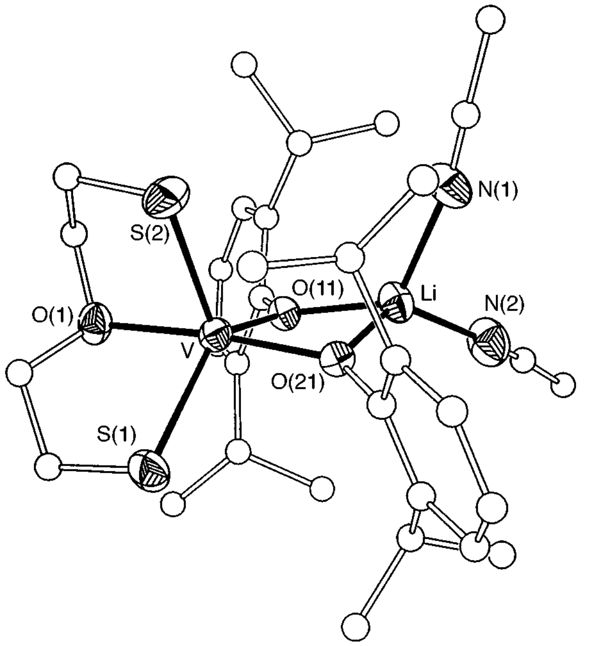

Fig. 1 The molecular structure of **2** (the displacement ellipsoids are drawn at the 30% probability level; the C bonded H atoms are excluded for clarity; the C atoms are represented by circles of arbitrary radii). Selected bond lengths (Å): V–S(1) 2.294(1), V–S(2) 2.286(2), V–O(1) 2.154(2), V–O(11) 1.917(2), V–O(21) 1.977(2), V–Li 2.830(5), Li–O(11) 1.942(6), Li(1)–O(21) 1.903(5), Li–N(1) 2.030(6), Li–N(2) 2.015(6).

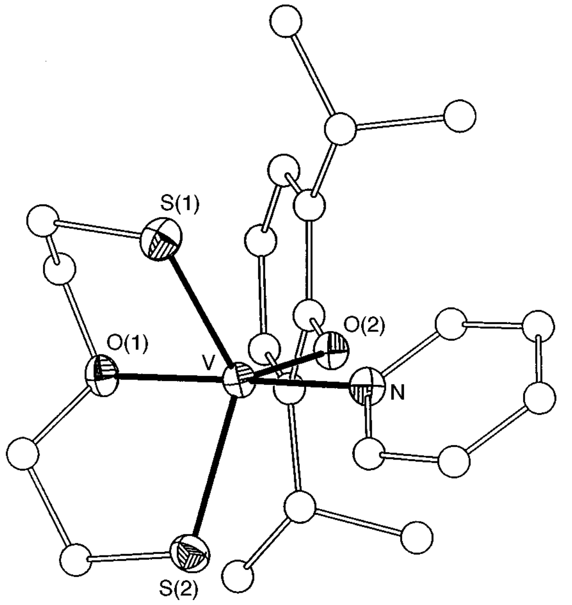

Fig. 2 The molecular structure of **3** (the displacement ellipsoids are drawn at the 30% probability level; the C bonded H atoms are excluded for clarity; the C atoms are represented by circles of arbitrary radii). Selected bond lengths (Å): V–S(1) 2.2970(9), V–S(2) 2.2987(8), V–O(1) 2.1195(14), V–O(2) 1.8619(13), V–N 2.1306(17).

Table 1 Polymerization[a] of ethylene with vanadium–$MgCl_2$–$AlEt_2Cl$ catalysts

Catalyst system	T/K	Productivity[b]/ kg(g V h)$^{-1}$	M_w/M_n	d/g cm^{-3}
1/$MgCl_2$/$AlEt_2Cl$	323	39	2.7	0.964
3/$MgCl_2$/$AlEt_2Cl$	323	20	3.8	0.961

[a] *Conditions:* $[V]_0 = 0.02$ mmol dm^{-3}, $[Al] = 10$ mmol dm^{-3}, Mg : V = 10, $P_{ethylene} = 0.6$ MPa. [b] Mass in kg of polymer formed per g of vanadium atoms in 1 h.

distance is also near the values observed in the other V^{III}–pyridine complexes.[11]

Compounds **1** and **3**, in combination with $AlEt_2Cl$ and $MgCl_2$, are highly active towards ethylene polymerization.[16] Yields and polymer characterization data are listed in Table 1. The amount of polyethylene (PE) produced by the catalysts is comparable to the catalyst based on VCl_3.[17] The molecular weight distribution M_w/M_n of the PE obtained in the first catalytic system is < 3, and in the second one is > 3. These findings indicate that the polymerization process in **1**/$MgCl_2$/$AlEt_2Cl$ proceeds on a single vanadium site in a homogeneous system, however for **3**/$MgCl_2$/$AlEt_2Cl$ a heterogeneous system appears to operate. Hence, the catalytic activity of the **1**/$MgCl_2$/$AlEt_2Cl$ system is almost twice that of the **3**/$MgCl_2$/$AlEt_2Cl$ system.

To our knowledge complexes **1** and **3** represent the first examples of vanadium-thiolate catalyst precursors for ethylene polymerization. We suggest that the $V\{O(CH_2CH_2S)_2\}$ moiety is maintained in the catalyst assembly and that the geometry of such catalytic species plays an important role in determining the reactivity. It is worth noting that vanadium catalysts are very important in ethylene–propylene rubber production.[18]

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Notes and references

† *Crystal data for* **2** *and* **3**: The crystals were sealed in glass capillaries under a dinitrogen stream. Preliminary examination and data collections were carried out on a KUMA KM-4 four-circle diffractometer[19] using graphite-monochromated Mo-Kα radiation (0.71073 Å) with ω-2θ scan mode. The structures were solved by direct methods (SHELXS97)[20] and refined on F^2 by full-matrix least-squares (SHELXL97).[21] The carbon bonded H-atoms were included in calculated positions and refined using a riding model with isotropic displacement parameters equal to 1.2 U_{eq} of the attached C atom.

Crystal structure analyses: **2**: $C_{32}H_{48}LiN_2O_3S_2V$, $M = 630.72$, monoclinic, space group $C2/c$, $a = 27.297(5)$, $b = 18.880(4)$, $c = 17.444(3)$ Å, $\beta = 126.76(3)$, $U = 7203(2)$ Å^3, $Z = 8$, $D_c = 1.163$ Mg m^{-3}, $\mu = 0.422$ mm^{-1}, $F(000) = 2688$. A total of 4086 reflections with $2\theta \leqslant 50°$ were collected, of which 3463 had $I \geqslant 2\sigma(I)$. Final residuals are $R_1 = 0.0357$, $wR_2 = 0.1007$ and GOF = 1.075 for 380 variables.

3: $C_{21}H_{30}NO_2S_2V$, $M = 443.52$, monoclinic, space group $P2_1/n$, $a = 10.022(3)$, $b = 12.156(4)$, $c = 18.628(4)$ Å, $\beta = 98.44(3)°$, $U = 2244.8(11)$ Å^3, $Z = 4$, $D_c = 1.312$, $\mu = 0.643$ mm^{-1}, $F(000) = 936$. A total of 3526 reflections with $2\theta \leqslant 50°$ were collected, of which 3108 had $I \geqslant 2\sigma(I)$. Final residuals are $R_1 = 0.0269$, $wR_2 = 0.0760$ and GOF = 1.124 for 248 variables.

CCDC 182/1237. See http://www.rsc.org/suppdata/cc/1999/1015/ for crystallographic files in .cif format.

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