Syntheses and Structural Characterization of Vanadium and Aluminum Thiolates

Zofia Janas,[†] Lucjan B. Jerzykiewicz,[†] Szymon Przybylak,[†]
Raymond L. Richards,[‡] and Piotr Sobota*,[†]

*Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie Street,
Wrocław 50383, Poland, and Department of Chemistry, Physics and Environmental Studies,
University of Sussex, Brighton, BN1 9RQ, U.K.*

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Stoichiometric reaction of $[VCl(DIPP)_2(THF)_2]$ (DIPP = 2,6-diisopropylphenoxide) with 2,2′-oxydiethanethiol $O(CH_2CH_2SH)_2$ in CH_3CN yields two products: $[V^{IV}\{O(CH_2CH_2S)_2\}_2]$, **1**, and $[V^{II}(CH_3CN)_6][V^{III}Cl_2\{O(CH_2CH_2S)_2\}]_2$, **2**. Compounds **1** and **2** were identified by conventional methods, including single-crystal X-ray diffraction for **2**. Compound **2** reacts with Li(DIPP) and Na(PyT) (PyT = pyridine-2-thiolate) in the presence of TMEN (TMEN = *N*,*N*,*N*′,*N*″-tetramethylethylenediamine) to give $[V^{II}(\mu\text{-DIPP})_4Li_2(THF)_4]$, **3**, $[V^{III}(\mu\text{-DIPP})_2\{O(CH_2CH_2S)_2\}Li_4(THF)_2]$, **4**, $[V^{II}(PyT)_2(TMEN)]$, **5**, and $[V^{III}(\mu\text{-PyT})_2\{O(CH_2CH_2S)_2\}Na(THF)_2]$, **6**. When combined with an aluminum activator and $MgCl_2$, compound **2** forms an active catalyst for ethylene polymerization. The interaction of **2** with an excess of $Al(CH_3)_3$ causes $\{O(CH_2CH_2S)_2\}^{2-}$ ligand abstraction from the vanadium center to give $[V_2(\mu\text{-O})Cl_4(THF)_6]$, **7**, and the organoaluminum compound $[Al_2\{\mu,\eta^3\text{-}(OCH_2CH_2SCH_2CH_2S)\}_2(CH_3)_2]$, **8**. The crystal structure of **8** showed it to be a dimer with aluminum atoms bridged by two alkoxo oxygen atoms from the ligand $\{OCH_2CH_2SCH_2CH_2S\}^{2-}$, formed by transformation of the starting $\{O(CH_2CH_2S)_2\}^{2-}$ ligand under the influence of $Al(CH_3)_3$.

Introduction

Vanadium catalysts are widely used for the industrial production of ethylene−propylene−diene elastomers (EPDM).[1] Well-known industrial catalyst precursors are the coordinatively saturated V(III) complexes [V(β-diketonate)$_3$]. It is well established that vanadium(II) species, which typically result in catalyst failure and deactivation, are largely produced by the action of the aluminum cocatalyst during the polymerization process and are a direct consequence of ligand abstraction by the cocatalyst.[2] The employment of catalyst reactivators (halocarbons) restores the trivalent oxidation state of vanadium and probably reforms the catalyst via ligand scrambling.[3] We found that alkoxo-vanadium(III) and -(IV) and aryloxo-vanadium(III) and -(V) complexes, in combination with an aluminum cocatalyst and $MgCl_2$,[4] are highly active toward ethylene polymerization.[5,6] These findings were successfully extended to dithiolatovanadium(III) compounds, which are the first examples of vanadium-thiolate catalyst precursors for ethylene polymerization.[7] This paper is a continuation of our study in this area and describes the synthesis and structural characterization of a novel mixed-valent vanadium(II)/(III) complex, $[V(CH_3CN)_6][VCl_2\{O(CH_2CH_2S)_2\}]_2$, **2**, together with its reactivity toward phenolate, thiolate, and $Al(CH_3)_3$ reagents. A preliminary ethylene polymerization test on **2**/$AlEt_2Cl/MgCl_2$ is reported as well.

Experimental Section

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. 2,6-Diisopropylphenol (DIPPH), 2,2′-oxydiethanethiol [$O(CH_2CH_2SH)_2$], pyridine-2-thiol (PytH), *N*,*N*,*N*′,*N*″-tetramethylethylenediamine (TMEN), and $Al(CH_3)_3$ (97%) were purchased from Aldrich. $[VCl(DIPP)_2(THF)_2]$[6] and Na(PyT)[8] were prepared by the literature methods. Li(DIPP) was prepared by the reaction of n-BuLi with DIPPH in hexane. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer in Nujol mulls. NMR spectra were performed on a Bruker ESP 300E spectrometer. Magnetic measurements

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* Corresponding author. E-mail: plas@wchuwr.uni.wroc.pl.

[†] University of Wrocław.

[‡] University of Sussex.

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were carried out with a Gouy balance. Magnetic moments were calculated following standard methods,[9] and corrections for underlying diamagnetism were made with Pascal's constants.[10]

Synthesis of [V{$O(CH_2CH_2S)_2$}$_2$], 1, and [V(CH_3CN)$_6$][VCl_2{$O(CH_2CH_2S)_2$}$_2$]$_2$, 2. To a solution of [VCl(DIPP)$_2$(THF)$_2$] (1.5 g, 2.4 mmol) in CH_3CN (30 mL) was added $O(CH_2CH_2SH)_2$ (0.3 mL, 2.4 mmol). The solution turned immediately red-violet, and after stirring at room temperature for 24 h an olive **1** precipitated. It was filtered off, washed with diethyl ether (3 × 5 mL), and dried in vacuo. Yield: 0.13 g, 17%. Anal. Calcd (Found) for $C_8H_{16}O_2S_4V$: C 29.71 (29.10), H 4.99 (4.58), S 39.65 (35.9). IR (Nujol mull, cm^{-1}): ν 1284 (m), 1260 (w), 1228 (w), 1202 (w), 1148 (w), 1068 (s), 1052 (m), 974 (s), 952 (m), 838 (w), 802 (w), 765 (w), 742 (w), 608 (w), 536 (w), 374 (m), 330 (s). $\mu_{eff} = 1.78-2.22\ \mu_B$ (77−297 K).

The complex **2** was isolated from the filtrate by evaporating the solvent to give an oily residue. This was washed with hexane (2 × 10 mL), to remove DIPPH, and dried in vacuo to give solid **2**. The yield of crude **2** was 1.46 g, 75%. Crystals suitable for X-ray study were obtained from a concentrated solution of **2** in CH_3CN at 273 K. Anal. Calcd (Found) for $C_{20}H_{34}Cl_4N_6O_2S_4V_3$: C 29.60 (29.85), H 4.23 (4.10), N 10.36 (9.10), S 15.77 (16.07). IR (Nujol mull, cm^{-1}): ν 2311 (s), 2281 (s), 1291 (s), 1261 (m), 1209 (m), 1172 (m), 1105 (w), 1052 (s), 1045 (s), 1009 (s), 974 (m), 940 (m), 930 (m), 725 (m), 673 (w), 552 (m), 472 (m), 406 (s), 375 (s), 341 (s). $\mu_{eff} = 2.99\ \mu_B$.

Reaction of 2 with Li(DIPP). Li(DIPP) (1.8 g, 9.83 mmol) was added to a solution of compound **2** (1 g, 1.23 mmol) in THF (30 mL). After the reaction mixture was stirred for 12 h, the green-brown solution was evaporated to dryness and the residual product extracted with hexane (25 mL). The yellow-green extract was concentrated to 10 mL and allowed to stand at 273 K for 2 days. Light yellow-green crystals of [V^{II}(μ-DIPP)$_4$Li$_2$(THF)$_4$], **3**, were collected by filtration and dried in vacuo. Yield: 0.45 g, 40%. The crude red-brown solid remaining after extraction of **3** was dissolved in CH_2Cl_2 (30 mL) and filtered to remove LiCl, and the filtrate was evaporated to dryness. The residual solid was recrystallized from THF/hexane (1:2, 10 mL) to give pink-red microcrystalline [V^{III}(μ-DIPP)$_2${$O(CH_2CH_2S)_2$}Li(THF)$_2$], **4**. Yield: 1.02 g, 60%. Both compound **3**[11] and compound **4**[7] were identified by comparison of their spectroscopic data, crystallographic cell parameters, and combustion analysis data with those described in the literature.

Reaction of 2 with Na(PyT). A solution of Na(PyT) (1.80 g, 13.6 mmol) in CH_3CN (20 mL) was added to a stirred, violet solution of **2** (1.84 g, 2.26 mmol) in CH_3CN (30 mL). The solution rapidly turned deep-red. The mixture was stirred for 12 h and filtered to remove NaCl, and the solvent was removed in vacuo to give a red-brown solid. This solid was dissolved in THF (30 mL) and stored at 289 K for 2 days. The resultant red crystals of [V^{III}(μ-PyT)$_2${$O(CH_2CH_2S)_2$}Na(THF)$_2$], **6**, were collected by filtration and recrystallized from THF/hexane (1:1) (20 mL) at room temperature. Yield: 1.52 g, 60%. Anal. Calcd (Found) for $C_{22}H_{32}O_3N_2S_4NaV$: C 45.95 (45.01), H 5.10 (4.94), N 4.87 (4.70), S 22.32 (21.98). IR (Nujol mull, cm^{-1}): ν 1578 (s), 1544(s), 1438 (s), 1416 (s), 1356 (m), 1296 (m), 1260 (m), 1242 (m), 1136 (s), 1096 (s), 1052 (s), 1012 (m), 896 (m), 758 (s), 752 (s), 672 (m), 648 (m), 488 (w), 476 (w), 456 (w), 429 (w), 412 (w), 352 (m), 336 (m), 316 (s), 290 (m). $\mu_{eff} = 2.71\ \mu_B$.

TMEN was added to the brown filtrate remaining after separation of **6**, and the resulting deep-red solution was stirred for 1 h. Then, the solvent was removed in vacuo to give a deep purple solid. Yield: 0.21 g, 25%. Dark red crystals of [V^{II}(PyT)$_2$(TMEN)], **5**, were obtained from a THF solution layered with hexane. Compound **5** was identified by comparison of its spectroscopic and other data with those described in the literature.[8]

Table 1. Crystallographic Collection and Refinement Parameters for 2 and 8

	2	**8**
empirical formula	$C_{20}H_{34}Cl_4N_6O_2S_4V_3$	$C_{10}H_{22}Al_2O_2S_4$
fw	813.43	356.48
cryst dimens, mm^3	0.5 × 0.3 × 0.3	0.6 × 0.4 × 0.4
temp, K	299(1)	100.0(5)
wavelength, Å	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	8.031(2)	8.031(2)
b, Å	8.430(2)	14.119(3)
c, Å	13.743(3)	14.372(3)
α, deg	100.00(3)	90
β, deg	95.60(3)	93.65(3)
γ, deg	91.40(3)	90
volume, Å^3	911.1(4)	1626.3(6)
Z	1	4
calcd density, g/cm^3	1.482	1.456
abs coeff, mm^{-1}	1.303	0.684
abs corr	COSABS99, Starynowicz	COSABS99, Starynowicz
transmission (max, min)	0.732, 0.603	0.978, 0.430
scan mode	$\omega-2\theta$	$\omega-2\theta$
F(000)	413	752
θ range for collection, deg	2.46−25.04°	2.02−25.09°
index ranges	$0 \le h \le 8$ $-10 \le k \le 9$ $-16 \le l \le 16$	$0 \le h \le 9$ $0 \le k \le 16$ $-17 \le l \le 16$
no. of reflns collected	2748	3001
no. of indep reflns	2554	2837
R(int)	$R(int) = 0.0289$	$R(int) = 0.0107$
no. of data/restraints/params	2554/0/181	2837/0/187
goodness-of-fit on F^2	1.040	1.048
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0381, wR2 = 0.1010	R1 = 0.0302, wR2 = 0.0800
R indices (all data)[a]	R1 = 0.0734, wR2 = 0.1181	R1 = 0.0406, wR2 = 0.0855
largest diff peak, e/Å^3	0.467	0.412
largest diff hole, e/Å^3	−0.400	−0.530

[a] $R1 = \Sigma(F_o - F_c)/\Sigma F_{o;}$ $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Reaction of 2 with $Al(CH_3)_3$. A suspension of **2** (1 g, 1.23 mmol) in toluene (30 mL) was treated with $Al(CH_3)_3$ (1.59 mL, 16.6 mmol) at 273 K. The mixture was allowed to warm to room temperature, and the stirring was continued for 6 h. The resulting a dark brown solid was filtered off, washed with toluene (3 × 5 mL), and dried under vacuum. Redissolving the solid in THF (20 mL) turned the color violet-red. After filtration and concentration to small volume, the resulting solution was allowed to stand at 273 K for several days, during which time violet crystals of [V_2(μ-O)Cl_4(THF)$_6$], **7**, separated. Yield: 0.26 g, 50%. Compound **7** was identified by comparison of its spectroscopic and other data with those described in the literature.[12]

The dark brown solid obtained from a separate experiment analogous to that above [1.2 g of **2**, 1.9 mL, 19.9 mmol of $Al(CH_3)_3$] was extracted with CH_3CN (40 mL). The resulting light brown solution was concentrated to 10 mL and allowed to stand at room temperature. After 1 day [Al_2{μ,η^3-($OCH_2CH_2SCH_2CH_2S$)}$_2$(CH_3)$_2$], **8**, separated as a colorless, microcrystalline solid. Yield: 0.19 g, 43%. Anal. Calcd (Found) for $C_{10}H_{22}O_2S_4Al_2$: C 33.71 (33.9), H 6.17 (5.98), S 35.99 (35.01). IR (Nujol mull, cm^{-1}): ν 1298 (w), 1282 (m), 1264 (m), 1188 (s), 1070 (s), 1026 (s), 958 (m), 924 (w), 850 (m), 688 (s), 658 (s), 608 (s), 514 (m), 444 (m), 404 (m), 382 (m). ^1H NMR (CD_3CN): δ 3.89 (t, 2H, OCH_2), 2.75 (m, 6H, SCH_2), −0.87 (s, 3H, $AlCH_3$).

Synthesis of [Al_2{μ,η^3-($OCH_2CH_2SCH_2CH_2S$)}$_2$(CH_3)$_2$], 8. To a solution of $Al(CH_3)_3$ (2 mL, 13.5 mmol) in hexane (20 mL) at 273 K was added $O(CH_2CH_2SH)_2$ (0.55 g, 4 mmol) by

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syringe. Immediately, a white precipitate was formed. The mixture was stirred and warmed to room temperature, then CH_3CN (30 mL) was added. The resulting clear solution was allowed to stand overnight at room temperature, to give colorless, X-ray quality crystals of **8**. Yield: 0.68 g, 84%. Spectroscopic data for **8** prepared by this route were identical to those described above.

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 **2** (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 $AlEt_2Cl$ (20 mmol) for 15 min at 323 K under argon to form the active catalyst. The polymerization of ethylene was carried out at 303−343 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.

X-ray Crystallography. A crystal of **2** was sealed in a glass capillary under a dinitrogen stream, whereas a crystal of **8** was mounted on glass fiber and then flash-frozen to 100 K (Oxford Cryosystem-Cryostream Cooler). For both compounds preliminary examination and intensity data collections were carried out on a KUMA KM-4 four-circle diffractometer using graphite-monochromated Mo Kα radiation. Details on crystal data, data collection, and some features of the structure refinement are summarized in Table 1.

Results and Discussion

The reaction of $[VCl(DIPP)_2(THF)_2]^6$ with 1 equiv of $O(CH_2CH_2SH)_2$ in CH_3CN afforded after workup two products: an olive noncrystalline complex, $[V\{O(CH_2CH_2S)_2\}_2]$, **1** (yield; 17%), and red-violet crystals of $[V(CH_3CN)_6][VCl_2\{O(CH_2CH_2S)_2\}]_2$, **2** (yield 75%) (eq 1).

$$\begin{array}{c} 4[VCl(DIPP)_2(THF)_2] + 4O(CH_2CH_2SH)_2 \\ \Big\downarrow \, CH_3CN \\ \underset{\mathbf{1}}{[V\{O(CH_2CH_2S_2)\}_2]} + \underset{\mathbf{2}}{[V(CH_3CN)_6][VCl_2\{O(CH_2CH_2S)_2\}]_2} + 8DIPPH \end{array} \qquad (1)$$

Compound **1** is insoluble in organic solvents and attempts to obtain it in a crystalline form failed. It was identified by elemental analysis, IR spectroscopy, and magnetic susceptibility data. Compound **1** shows a temperature-dependent magnetic moment with μ_{eff} per V atom varying from 2.22 μ_B at 297 K to 1.78 μ_B at 77 K. The solid-state EPR spectrum of **1** exhibits a broad line ($\Delta H = 86$ G, $g = 1.974$) with eight principal lines (^{51}V, $I = 7/2$). This suggests weak antiferromagnetic coupling between the vanadium(IV) atoms. The IR spectrum of **2** shows characteristic modes of coordinated CH_3CN molecules at 2311 and 2281 cm^{-1} [ν(CN)] and bands at 552, 472 and 406, 375 cm^{-1}, assigned to ν(V−S) and ν(V−Cl), respectively. The temperature-independent magnetic moment of **2** (2.99 μ_B) per vanadium atom and the X-ray crystal structure are consistent with two d^2 and one d^3 vanadium centers which are noninteracting. The crystals of **2** consist of a cation $[V^{II}(CH_3CN)_6]^{2+}$ and an anion $[V^{III}Cl_2\{O(CH_2CH_2S)_2\}]^-$ in a 1:2 molar ratio. The structure of the cation is well known.[13] The molecular structure of the anion is shown in Figure 1, and selected bond lengths and angles are shown in Table 2. The anion of **2** contains a pentacoordinate V(III) center adopting a slightly distorted trigonal bipyramidal geometry. Two sulfur atoms from the $\{O(CH_2CH_2S)_2\}^{2-}$ ligand and one chlorine atom Cl(2) occupy the equatorial positions. The second chlorine atom Cl(1) and the ether oxygen O(1) from the $\{O(CH_2CH_2S)_2\}^{2-}$ group fill the axial sites. The average V−S and V−O(1)$_{ether}$ bond distances 2.2848(15) and 2.148(3) Å, respectively, do not differ significantly from those found in $[V(\mu\text{-DIPP})_2\{O(CH_2CH_2S)_2\}Li(CH_3CN)_2]$ and $[V(DIPP)\{O(CH_2CH_2S)_2\}(NC_5H_5)]$ compounds.[7] The V−Cl(1) bond length 2.3443(17) Å is distinctly longer than the V−Cl(2) distance 2.2769(18) Å. This indicates differing relative trans influences of the Cl(1) and O(1)$_{ether}$ atoms of the $\{O(CH_2CH_2S)_2\}^{2-}$ ligand. Generally the V−Cl distances are comparable with corresponding distances in vanadium(III) chlorides.[14]

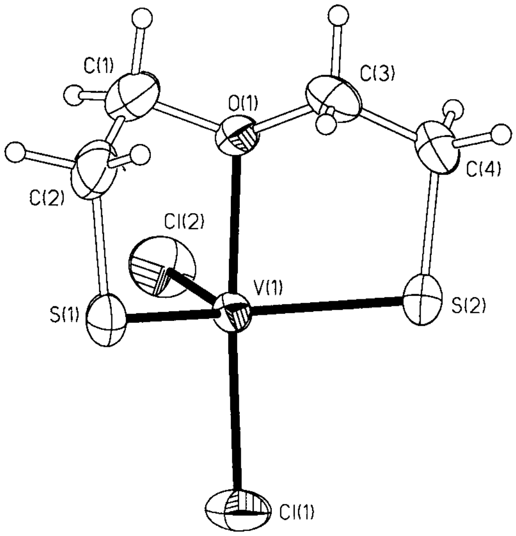

Figure 1. Structure of anion of **2** with atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 2[a]

V(1)−O(1)	2.148(3)
V(1)−Cl(2)	2.2769(18)
V(1)−S(2)	2.2823(15)
V(1)−S(1)	2.2873(17)
V(1)−Cl(1)	2.3443(17)
V(1)−Cl(2)	2.2769(18)
O(1)−V(1)−Cl(2)	89.73(11)
O(1)−V(1)−S(2)	82.10(9)
Cl(2)−V(1)−S(2)	119.61(7)
O(1)−V(1)−S(1)	82.93(11)
Cl(2)−V(1)−S(1)	117.67(7)
S(2)−V(1)−S(1)	120.35(6)
O(1)−V(1)−Cl(1)	172.35(11)
Cl(2)−V(1)−Cl(1)	97.88(7)
S(2)−V(1)−Cl(1)	93.44(6)
S(1)−V(1)−Cl(1)	94.09(6)

[a] Symmetry code: (a) $-x$, $1 - y$, $-z$.

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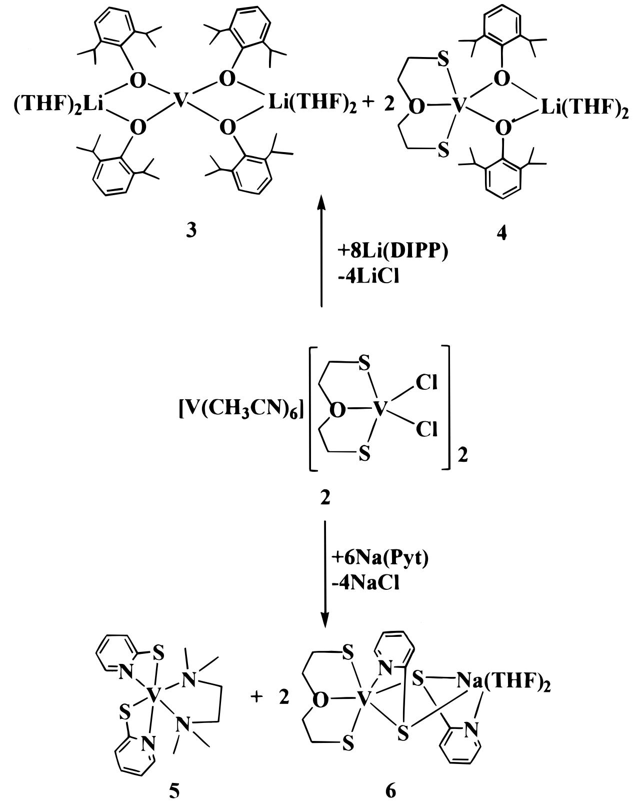
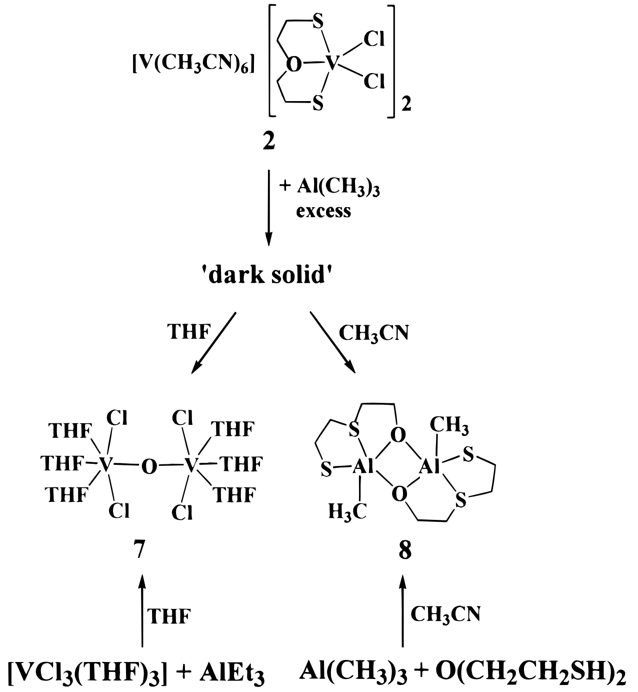
Scheme 1



Since chloride is present at the active center of many vanadium chloride-based catalysts,[15] the anion of compound **2**, having two mutualy cis chlorine atoms, seemed to be potentially attractive as a precatalyst of the ethylene polymerization process. Cossee[16] first proposed a simple concept to elucidate the olefin polymerization mechanism by assuming the formation of metal alkyls at the catalyst center by interaction of metal chlorides with alkylating agents. A number of possible routes to substitution of chlorine atoms in the anion of **2** have been studied, including the interaction of **2** with the standard alkylating agents LiR, RMgCl, R_2Mg, and R_2Zn (R = CH_3, C_2H_5, $CH_2C_6H_4$) using a wide range of solvents and reaction conditions. There was, however, no evidence from any of the reactions to suggest that clean alkylation had taken place. The only successful route to substitution of chloride ligands in the anion of **2** was the use of lithium and sodium salts of 2,6-diisopropylphenolate (DIPP) and 2-pyridinethiolate (PyT), respectively, as is shown in Scheme 1. Straightforward chloride replacement reactions by the use of Li(DIPP) and Na(PyT) salts modified the arrangement around the vanadium center in the anion of **2**. The cation and the anions of **2** appear to form products independently. Three of the products, $[V^{II}(\mu\text{-DIPP})_4Li_2(THF)_4]$, **3**,[11] $[V^{III}(\mu\text{-DIPP})_2\{O(CH_2CH_2S)_2\}Li(THF)_2]$, **4**,[7] and $[V^{II}(PyT)_2(TMEN)]$, **5**,[8] are clearly known and were identified by comparison of their properties with those described in the literature. The complex $[V(\mu\text{-PyT})_2\{O(CH_2CH_2S)_2\}Na(THF)_2]$, **6**, is new and was identified by elemental analysis, spectroscopic data, and magnetic susceptibility. Its structure (Scheme 1) is proposed by analogy with the compound $[V(\mu\text{-PyT})_2(PyT)_2Na(THF)_2]$ described by Christou at al.[8]

Scheme 2



In view of the failure to substitute the chloride ligands in the anion of compound **2** by alkyl groups we turned to careful examination of the interaction of compound **2** with the aluminum cocatalyst (Scheme 2). The reaction of **2** with an excess of $Al(CH_3)_3$ in toluene gave a "dark solid" insoluble in hydrocarbons. Treatment of this solid with THF yielded a red-violet solution from which were obtained bright violet crystals of $[V_2(\mu\text{-O})Cl_4(THF)_6]$, **7**, containing vanadium in the formal oxidation state +3, as reported earlier by Bird at al.[12] When the dark solid was extracted with acetonitrile, a light brown solution was obtained, from which a white crystalline compound, $[Al_2\{\mu,\eta^3\text{-}(OCH_2CH_2SCH_2CH_2S)\}_2(CH_3)_2]$, **8**, was isolated. This species was also conveniently prepared by the methane elimination reaction of an excess of $Al(CH_3)_3$ with $O(CH_2CH_2SH)_2$ in CH_3CN. Compound **8** is very sensitive in the solid state and can be stored only in solution. In the ^1H NMR spectrum of **8** the absence of an SH resonance and the presence of a sharp resonance (δ −0.89) upfield for the alkyl group attached to aluminum provide good evidence for $Al(CH_3)$ coordination at the thiolato ligand. However, resonances from this coordinated thiolate ligand differ significantly from the parent $O(CH_2CH_2S)_2{}^{2-}$ ligand. The crystal structure analysis of **8** solved this problem, as is shown in Figure 2. Selected bond lengths and angles are depicted in Table 3. The central structural unit of compound **8** is a planar four-membered ring composed of two aluminum atoms and the two bridging oxygen atoms from the $(OCH_2CH_2SCH_2CH_2S)^{2-}$ ligand. The five-coordination sphere of the aluminum atoms is completed by two different sulfur atoms, thiolate and thioether from the $(OCH_2CH_2SCH_2CH_2S)^{2-}$ ligand, and a carbon atom from the CH_3 group. The Al−μ-O bond distances range from 1.8295(17) to 1.8762(17) Å and are similar to other alkoxides and less than the Al−O distances observed in the monomeric adducts.[17] The average Al−$S_{thiolato}$

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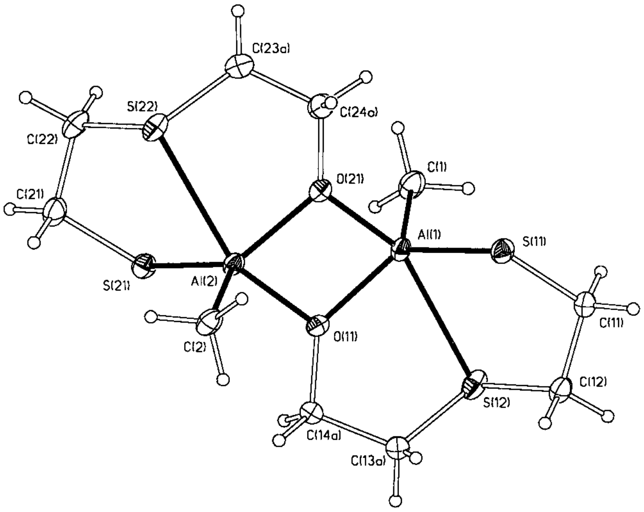

Figure 2. Molecular structure of **8** with atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. The second position of the disordered atoms are excluded for clarity.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 8

Al(1)−O(11)	1.8295(17)
Al(1)−O(21)	1.8749(17)
Al(1)−C(1)	1.940(3)
Al(1)−S(11)	2.2442(10)
Al(1)−S(12)	2.6732(10)
Al(2)−O(21)	1.8362(18)
Al(2)−O(11)	1.8762(17)
Al(2)−C(2)	1.947(2)
Al(2)−S(21)	2.2562(10)
Al(2)−S(22)	2.6336(10)
Al(1)···Al(2)	2.8859(12)
O(11)−Al(1)−O(21)	77.73(7)
O(11)−Al(1)−C(1)	120.83(10)
O(21)−Al(1)−C(1)	103.17(10)
O(11)−Al(1)−S(11)	117.21(7)
O(21)−Al(1)−S(11)	98.74(6)
C(1)−Al(1)−S(11)	120.88(9)
O(11)−Al(1)−S(12)	78.90(6)
O(21)−Al(1)−S(12)	155.48(6)
C(1)−Al(1)−S(12)	95.08(9)
S(11)−Al(1)−S(12)	85.43(3)
O(21)−Al(2)−O(11)	77.54(7)
O(21)−Al(2)−C(2)	119.48(10)
O(11)−Al(2)−C(2)	105.87(9)
O(21)−Al(2)−S(21)	117.94(7)
O(11)−Al(2)−S(21)	95.79(6)
C(2)−Al(2)−S(21)	121.57(9)
O(21)−Al(2)−S(22)	80.01(6)
O(11)−Al(2)−S(22)	155.10(6)
C(2)−Al(2)−S(22)	94.45(8)
S(21)−Al(2)−S(22)	85.31(3)

bond distance 2.2502(10) Å is similar to that found in monomeric tetrahedral compounds such as [Al(^{t}Bu)$_2$(SCH$_2$CH$_2$NR$_2$)] [2.262(2) Å for R = Me and 2.272(4) Å for R = Et],[18] somewhat shorter than observed in the trigonal bipyramidal complex [AlH(SCH$_2$CH$_2$NEt$_2$)$_2$] [2.175(2) and 2.182(4) Å][19] and distinctly shorter than Al−μ-S bridges in [Al$_2$(μ-SC$_6$F$_5$)$_2$Me$_4$] [2.405(2) Å].[20] The average Al−C bond length 1.944(2) Å is clearly within the range expected for Al−C terminal bond distances.[17,21] The formation of **8** containing alkoxo-oxygen bridges is the result of unexpected rearrangement of the (SCH$_2$CH$_2$OCH$_2$CH$_2$S)$^{2-}$ ligand under the influence of Al(CH$_3$)$_3$; that is, the ether oxygen became alkoxide and one thiolato-sulfur changed into thioether, producing the new ligand (OCH$_2$CH$_2$SCH$_2$CH$_2$S)$^{2-}$. To confirm that this rearrangement was not accidental, a number of crystals obtained from separate experiments were examined. In all cases the formation of **8** was confirmed. The alkoxo character of the bridging atoms in **8** was also confirmed chemically. When compound **4** was treated with pyridine, the formation of monomeric species was not observed. To our knowledge this is the first example of such rearrangement for the O(CH$_2$CH$_2$S)$_2$$^{2-}$ ligand, in contrast with the thiadithiolate analogue S(CH$_2$CH$_2$S)$_2$$^{2-}$, for which the facile C−S(thia) bond cleavage is known.[22]

A preliminary polymerization test on compound **2** in combination with AlEt$_2$Cl and MgCl$_2$ gave 5 kg of polyethylene per g V h^{-1} (Mg V = 10, [V]$_0$ = 0.02 mmol dm^{-3}, and [Al] = 5 mmol dm^{-3}). This is 8- and 4-fold less when compared with a catalyst based on [V(μ-DIPP)$_2${O(CH$_2$CH$_2$S)$_2$}Li(THF)$_2$] and [V(DIPP){O(CH$_2$CH$_2$S)$_2$}(py)], respectively.[7] The question arises, what is the reason for the different catalytic activity of those dithiolate precatalysts? We suggest that the activiy of these compounds depends mainly on the nature of ligands which are responsible for the solubility of active catalysts. The results of the interaction of Al(CH$_3$)$_3$ with compound **2** indicate that abstraction of the {O(CH$_2$CH$_2$S)$_2$}$^{2-}$ ligand from the vanadium(III) coordination sphere occurs, and as a consequence a V(II) chloride species is formed. In the case of the compounds [V(μ-DIPP)$_2${O(CH$_2$CH$_2$S)$_2$}Li(THF)$_2$] and [V(DIPP){O(CH$_2$CH$_2$S)$_2$}(py)] the migration of the {O(CH$_2$CH$_2$S)$_2$}$^{2-}$ ligand from the vanadium(III) center, produces a {V^{II}(DIPP)} species which completely disproportionates to give {V^{III}(DIPP)} species, known to be very well soluble in hydrocarbons.[23]

Conclusions

The reaction of [VCl(DIPP)$_2$(THF)$_2$] with O(CH$_2$CH$_2$SH)$_2$ results in the formation of the mixed-valence V(II)/V(III) complex [V(CH$_3$CN)$_6$][VCl$_2${O(CH$_2$CH$_2$S)$_2$}]$_2$, **2**. Attempts to substitute chloride in the anion of **2** by alkyl

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groups failed. However, chloride ligands are very easily substituted by the aryloxide and thiolate groups to form V(II) (**3**, **5**) and V(III) (**4**, **6**) compounds. Under the influence of an excess of $Al(CH_3)_3$, the abstraction and transformation of the $\{O(CH_2CH_2S)_2\}^{2-}$ ligand from the vanadium(III) center of **2** occurs, resulting in the formation of the dimeric organoaluminum complex **8**. This result indicates that during the catalytic cycle the $\{O(CH_2CH_2S)_2\}^{2-}$ ligand migrates to an aluminum atom of the activator and a V(II) species is formed, which is considered to be inactive in the ethylene polymerization process.[2]

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Supporting Information Available: Tables of crystal data, structure solution and refinement details, atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, and bond distances and angles for **2** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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