(2) The rate is approximately inversely proportional to $[HL]_{ad}$ and practically vanishes for large $[HL]_{ad}$.

These features strongly suggest that the process proceeds by ligand dissociation, followed by complex formation between FeL_2^+ and ascorbic acid and electron transfer inside this complex.

(3) Such a pathway is supported by the reaction orders. The initial rate in both organic solvents and micelles is first order with respect to iron(III) for $[Fe(III)] \lesssim 10^{-4}$ mol dm^{-3} and a large excess of ascorbic acid. At higher [Fe(III)] "saturation" with slower rate variation with [Fe(III)] appears. The rate dependence on the ascorbic acid concentration is "S-shaped", approaching a limiting value for large concentrations, but tends toward first-order dependence for small concentrations.

Ligand substitution is thus apparently of rather crucial importance in the release of iron from the micelle-trapped complex by reduction with ascorbic acid. The double-layer effects from the polar micelle surface groups will therefore exert a pronounced influence not only on the thermodynamic stability of the iron complex but also on the kinetics of the release by ascorbic acid reduction.

Registry No. TBH, 67009-50-1; ascorbic acid, 50-81-7.

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Synthesis and Characterization of an Oxygen-Bridged Vanadium(III) Dimer

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Dinuclear and polynuclear oxygen-bridged compounds of vanadium occur mainly in the higher valence states of the transition metal, primarily as oxides[1,2] and vanadates in aqueous solution,[3,4] while they are virtually unknown in nonaaqueous media.[5,6] For V(III) and lower oxidation states of V, a hydrolytic dimer, $V^{III}{-}O{-}V^{III}$, has been known to exist fleetingly in aqueous perchlorate solutions;[7–9] it is believed to be an intermediate in the oxidation of V(II) to V(III) (vide infra). Such a dimeric species, if definitively characterized, would give some insight into the bonding characteristics of V in its lower oxidation states. This is at present limited primarily due to the experimental difficulties encountered in working with the lower oxidation states of vanadium.[10,11] This paper reports the first isolation in crystalline form, to our knowledge, of the V(III) dimeric species $[(THF)_3Cl_2VOVCl_2(THF)_3]$. This was obtained as an isolable intermediate during the reduction of VCl_3 by triethylaluminum in tetrahydrofuran (THF).

Reaction of vanadium halides with metal alkyls is a frequently used and not always successful route to lower valence vanadium compounds,[12] the other methods commonly employed being electrochemical reduction[13,14] and the use of reducing agents such as zinc dust.[15] Reactions of this sort, which have been the subject of intense mechanistic study,[16] are frequently employed to obtain low-valence-state organometallic compounds of vanadium,[17,18] as well as to produce highly specific catalytic systems,[19] one of the most important of which are of course the Ziegler–Natta catalysts.[20,21] The precise nature of the stereospecific action of these catalysts is unfortunately still not too well understood today.[22] In addition, it is recognized that one of the most common poisons for these catalysts is molecular oxygen,[23,24] which sometimes turns up even in the most thoroughly purified organic solvents. The precise nature of the poisoning effect of molecular oxygen also remains poorly understood.[23] Since the reaction system described in this work (i.e. $VCl_3 + AlEt_3$ in THF) is capable of acting as a highly stereospecific homogeneous Ziegler–Natta catalyst in hydrocarbon solvents,[25] it is believed that the results of the present paper may give some insight into this subject.

Experimental Section

All experiments were carried out under a dry N_2 or argon atmosphere by using standard Schlenkware, drybox, and vacuum-line techniques. Tetrahydrofuran (Fisher) was triply distilled over Na (under N_2) until a blue coloration was obtained with benzophenone and then redistilled under high vacuum. Dimethylformamide, diethyl ether, and other solvents (Fisher) were dried and deoxygenated in the customary manner.[26] $ZnEt_2$ was prepared from EtI–EtBr and a Zn–Cu couple as described elsewhere.[27] Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). IR measurements of solid samples, prepared as Nujol mulls between AgCl windows, were carried out on a Perkin-Elmer IR 599 (double-beam) spectrometer. UV–vis measurements of solutions under argon atmosphere were carried out on a Pye-Unicam SP8-100 (double-beam) spectrometer. High-purity VCl_3 and $AlEt_3$ (Alfa, Division of Ventron) were used as supplied by the manufacturer. EtI and EtBr (Fisher) were distilled under high vacuum prior to use.

$[(THF)_3Cl_2VOVCl_2(THF)_3]$ (A). Five milliliters of 0.1 M $AlEt_3$ in THF and 5 mL of 0.1 M VCl_3 in THF were cooled to ca. −50 °C (ether–liquid N_2 slush), and the VCl_3 solution was added slowly to the $AlEt_3$ with stirring (via syringe and septa). The initial brown coloration quickly turned to an intense violet on warming to ca. −35 °C. The reaction mixture was reduced to one-third of its original volume by high-vacuum distillation, and the contents were left at ca. −20 °C for 48 h, yielding crystals of A, which were washed with ether, recrystallized from THF, and dried in vacuo. Variation of the $AlEt_3/VCl_3$ ratio did not yield a different product. Compound A was obtained as brilliant violet crystals. UV–vis (nm): in THF, 487 (ε 631, CT), 600 (ε 149, $^4A_{2g} \rightarrow {}^4T_{1g}$, V(II)), 766 (ε 30); in CH_3CN, 487 (ε 600, CT), 680 (ε 70, $^4A_{2g} \rightarrow {}^4T_{1g}$, V(II)); in DMF, 482 (ε 4000

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Table I. Summary of Crystal Parameters and Intensity Data Collection

Crystal Parameters

cryst system	monoclinic	Z	4
space group	$C2/c$	d_{calcd}, g cm^{-3}	1.236
a, Å	19.181 (5)	temp, °C	22
b, Å	9.200 (5)	formula	$V_2Cl_4C_{24}H_{48}O_7$
c, Å	18.935 (5)	fw	692.34
β, deg	103.09 (1)	cryst dimens, mm	0.2 × 0.1 × 0.1
V, Å	3721 (1)		

Measurement of Intensity Data

diffractometer	Picker	refinement	block-diagonal least squares
radiation	Mo Kα (λ = 0.710 69 Å), graphite monochromated	no. of params	168
		R^a	0.097
unique reflcns	1518	$R_w{}^a$	0.048
obsd reflcns ($I > 3\sigma(I)$)	937	GOF^b	4.1

[a] Function minimized: $\Sigma w(|F_o| - |F_c|)^2$, $w = 1/(\sigma(F_o))^2$. $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = ((w(|F_o| - |F_c|)^2)^{1/2}$. [b] GOF = $(\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v))^{1/2}$; N_o and N_v are respectively the number of observations and the number of variables.

Table II. Positional Parameters, with Esd's, for $[(THF)_3Cl_2VOVCl_2(THF)_3]$

atom	x	y	z
V	0.0716 (1)	−0.0146 (4)	0.3275 (1)
Cl1	0.0191 (2)	0.1538 (5)	0.3965 (2)
Cl2	0.3540 (2)	0.3186 (5)	0.2180 (2)
OB	0.0000^a	−0.015 (2)	0.2500^a
O1	0.3376 (5)	0.484 (1)	0.0731 (5)
O2	0.1287 (5)	0.163 (1)	0.2899 (5)
O3	0.4718 (5)	0.307 (1)	0.1220 (4)
C1	0.2345 (7)	0.027 (2)	0.4290 (8)
C2	0.2741 (8)	−0.008 (3)	0.0035 (9)
C3	0.2222 (8)	0.011 (3)	0.0482 (8)
C4	0.1543 (8)	0.052 (2)	−0.0012 (7)
C5	0.1576 (8)	0.149 (2)	0.2243 (8)
C6	0.1596 (8)	0.305 (2)	0.1978 (8)
C7	0.1616 (9)	0.394 (2)	0.262 (1)
C8	0.1177 (8)	0.317 (2)	0.3060 (9)
C9	0.4521 (9)	0.157 (2)	0.1289 (9)
C10	0.4970 (9)	0.079 (2)	0.0865 (9)
C11	0.4381 (8)	0.168 (2)	0.412 (8)
C12	0.4609 (7)	0.322 (2)	0.4014 (7)

[a] Special position.

Table III. Relevant Bond Lengths and Angles, with Esd's, in $[(THF)_3Cl_2VOVCl_2(THF)_3]$

Distances (Esd), Å

V–Cl1	2.390 (6)	O2–C8	1.47 (2)
V–Cl2	2.384 (6)	O3–C9	1.44 (2)
V–OB	1.769 (5)	O3–C12	1.46 (2)
V–O1	2.26 (1)	C1–C2	1.45 (2)
V–O2	2.18 (1)	C2–C3	1.46 (2)
V–O3	2.16 (1)	C3–C4	1.47 (2)
O1–C1	1.43 (2)	C5–C6	1.51 (2)
O1–C4	1.44 (2)	C6–C7	1.46 (2)
O2–C5	1.48 (2)	C7–C8	1.49 (2)

Angles (Esd), deg

Cl1–V–Cl2	167.0 (2)	O2–V–O3	171.7 (3)
Cl1–V–OB	96.5 (4)	O1–V–Cl2	83.5 (3)
Cl1–V–O2	89.9 (3)	O1–V–O2	86.0 (4)
Cl1–V–O1	83.5 (3)	O1–V–OB	179.4 (5)
Cl1–V–O3	89.9 (3)	Cl2–V–O3	89.6 (4)
O2–V–O1	85.7 (4)	Cl2–V–OB	96.5 (4)
O2–V–Cl2	88.7 (3)	O3–V–OB	93.4 (5)
O2–V–OB	94.9 (5)		

CT), 678 (ϵ 500, $^4A_{2g} \rightarrow {}^4T_{1g}$). IR (cm^{-1}): 1455, 1372 ($\nu(CH_3)$, vs); 1072 (vs); 1035 (ν(C–O–C), m); 365 ($\nu(V–O_{THF})$).[28] Anal. Calcd for $V_2Cl_4C_{24}H_{48}O_7$ (mol wt 692.34): V, 14.72; Cl, 26.48; C, 41.64; H, 6.99; O (by difference), 10.17. Found: V, 14.35; Cl, 26.89; C, 41.47; H, 6.80; O (by difference), 10.49. Stability: extremely air-sensitive; prolonged stability only under Nujol kept in drybox; crumbled on exposure even in drybox (suspect loss of solvent from crystal lattice). Solubility: soluble in CH_3CN, CH_2Cl_2, CH_2ClCH_2Cl, and DMF (intense violet coloration in all); insoluble in benzene, hexane, and toluene; decomposes in CH_3OH and acetone.

[V(THF)$_4$ZnCl$_4$] (B). According to the procedure described above for A, 5 mL of 0.1 M $ZnEt_2$ in THF and 5 mL of 0.1 M VCl_3 in THF were reacted at −50 °C, to yield a bright violet solution and, after 2 days at −20 °C, purple-black crystals, insoluble in THF, with which they were washed prior to drying in vacuo. UV-vis (nm) (of reaction mixture in THF): 483 (ϵ 390), 600 (ϵ 72). IR (cm^{-1}): 1455, 1372 ($\nu(CH_3)$, vs); 1035 (ν(C–O–C), m–s), 1015 (s); 362 ($\nu(V–O_{THF})$, s). Anal. Calcd for $VZnCl_4C_{16}H_{32}O_4$ (mol wt 546.55): Zn, 11.96; V, 9.32; Cl, 25.95; C, 35.16; H, 5.9; O (by difference), 11.7. Found: Zn, 11.50; V, 9.39; Cl, 25.94; C, 35.09; H, 6.04; O (by difference), 12.04.

Gas Chromatographic Analyses. The reaction mixtures from the above syntheses were analyzed for dissolved product gases by using a computer-controlled Perkin-Elmer Sigma 2 gas chromatograph equipped with a stainless-steel column ($^1/_4$ in. × 6 ft.) packed with Chromosorb 102. The gases were collected in a liquid-N_2 trap by distillation on a high-vacuum line from the reaction mixture after removal of $AlEt_3$ and $ZnEt_2$ through an intermediate trap held at −50 °C. The injection-port temperature was 175 °C, the carrier-N_2 flowrate was 25 mL/min, and the column temperature was programmed as follows: initial, 70 °C; at 6 min a programmed increase of 30 °C/min to a final temperature of 200 °C. Table IV summarizes the results of the analyses.

Collection and Reduction of X-ray Data for [(THF)$_3$Cl$_2$VOVCl$_2$(THF)$_3$]. A summary of crystal and intensity collection data is presented in Table I. A crystal from the recrystallized batch of the compound (ca. 0.2 × 0.1 × 0.1 mm) was mounted in a capillary containing Nujol and sealed under partial vacuum; crystals mounted without Nujol did not last through the intensity data collection. A Picker four-circle diffractometer interfaced to a PDP 8/a minicomputer and employing the peak-search, centering, indexing, and data-collection program package of the National Research Council of Canada[29] was used. The θ–2θ scan mode was employed. The structure was solved by conventional heavy-atom techniques, the V atom being located by a Patterson synthesis. Block-diagonal least-squares refinement yielded the positions of all remaining non-H atoms. With isotropic thermal parameters, an R factor of 0.119 (0.127 weighted) was obtained, which with anisotropic refinement yielded final values of 0.097 unweighted and 0.047 weighted for the R factor.

Results and Discussion

Figure 1 shows the ORTEP diagram and labeling scheme for the molecule $[(THF)_3Cl_2VOVCl_2(THF)_3]$ (A). Table II lists the final positional parameters with esd's for the non-H atoms. Table III lists the important bonded contacts with esd's for A. The molecule is essentially a linear, oxygen-bridged dimer with the V atoms octahedrally coordinated (each to two Cl atoms and three THF groups) and V in a formal oxidation state of III with 14 electrons assignable to each V. The chlorines and THF's on one V are staggered with respect to those on the other V, with the Cl's bent away from the bridging oxygen. The V–Cl bond length (2.39 Å) compares favorably with the sum of the Bragg–Slater atomic radii[30] for V and Cl (1.35 and 1.00 Å) and with bond lengths obtaining in other, similar molecules.[31,32] The bending of the Cl's away from the bridging O causes the V–O bond for the main-axis THF (O1, 2.26 Å), to lengthen relative to that of the other THF oxygens (2.17 Å average). Using the method of Brown and Wu for calculation of bond orders to V–O bonds,[33] one obtains

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Table IV. Summary of Chromatographic Analyses: Percent Composition of Product Gases

gas	for VCl_3 + $ZnEt_2$ in THF	for VCl_3 + $AlEt_3$ in THF
butane	19.6	5.6
ethane	53.5	74.9
ethylene	26.9	19.5

an average value for the bond order of ca. 0.6 for the $V–O_{THF}$ bonds in A and a value of ca. 0.98 for the $V–O_B$ bond. The $V–O_B$ bond length (1.76 Å) compares favorably with those observed in compounds containing O-bridged vanadiums, e.g. NaV_2O_4F,[34] $Li_2V_2O_5$,[35] and α-$[Zn_3(VO_4)_2]$.[36]

The $V^{III}–O–V^{III}$ moiety was first observed by Newton and Baker[8,9] in a kinetic study of the reaction of V(II) and V(IV) as their perchlorates in acidic medium. They determined that the overall reaction

$$V^{2+} + VO^{2+} + 2H^+ \rightarrow 2V^{3+} + H_2O$$

proceeded via the conventional outer-sphere activated complex (35%) as well as through an intermediate, $(V–O–V)^{4+}$, possessing a characteristic and strong absorption at 425 nm. Swinehart[37] convincingly demonstrated the existence of the $(V–O–V)^{4+}$ moiety in a study of V(II) perchlorate oxidation by molecular oxygen and H_2O_2. A similarly structured Cr(III) moiety, $(Cr–O–Cr)^{4+}$, was observed by Ardon and Plane[38] upon oxidation of $Cr(ClO_4)_2$ by molecular oxygen. Two-electron acceptors such as Tl^{3+}, ClO_3^-, HClO, and $Cr_2O_7^{2-}$ gave identical results, but one-electron acceptors such as Fe^{3+}, Cu^{2+}, Cl_2, or Br_2 did not.[38,39] Gandeboeuf and Souchay[40] observed the species $[H_2O(CH_3COO)–V–O–V–(CH_3COO)_2]^+$ at low pH in acetate media, characterized by an identical, strong absorption at 425 nm, while $[VOV(H_2O)]^{4+}$ was observed in sulfate media. In the present work, the characteristic intense absorption band of the $(V–O–V)^{4+}$ moiety is observed for the title compound (A) at 487 nm in THF and CH_3CN and at ca. 482 nm in dimethylformamide (DMF) (see Experimental Section). It is possibly an internal CT transition within the $V^{III}–O–V^{III}$ moiety and could be mediatory in an exchange of the type $V^{III}–O–V^{III} \rightarrow V^{II}–O–V^{IV}$, of a sort observed in $NH_3Ru^{II}–O–V^{IV}(EDTA)$,[41] i.e. $Ru(d_{xy})$ $(B_2) \rightarrow VO^{2+}$ π^* (E). It is evident that in the present work an initial, reduced V(II) produced in THF by the action of $AlEt_3$ is quickly oxidized by "adventitious oxygen"[42,43] to VO^{2+}, which then reacts further with unoxidized V(II) to yield the observed $V^{III}–O–V^{III}$: this phenomenon has been observed for tungsten halides.[44]

An analysis for dissolved product gases was conducted to obtain more information on the reaction paths and is summarized in Table IV. It must be remembered that in reactions between a transition-metal halide and main-group-metal ethyls, β-elimination is the major source of ethylene and dinuclear elimination is the major source of butane, while H abstraction (from an intermediate transition-metal hydride or from other sources) is the major source of ethane.[45] It is also to be noted that alkylation of the transition metal proceeds more to completion with a less polar alkyl such as $ZnEt_2$ (vis-à-vis the more polar $AlEt_3$);[16,18] this is evident in the formulations of the products obtained in this work: $[(THF)_3Cl_2VOVCl_2(THF)_3]$ has two chloro groups still attached to the V, while $[V(THF)_4ZnCl_4]$ does not. The results of the gas analyses (Table IV)—i.e. an excess of butane and ethylene for $ZnEt_2$ over that for $AlEt_3$—are thus explained by assuming that alkylation of V has occurred to a greater extent when $ZnEt_2$ is used; dinuclear elimination and β-elimination from the V, leading to butane and ethylene, respectively, are then more likely to occur for the $ZnEt_2$ reaction.

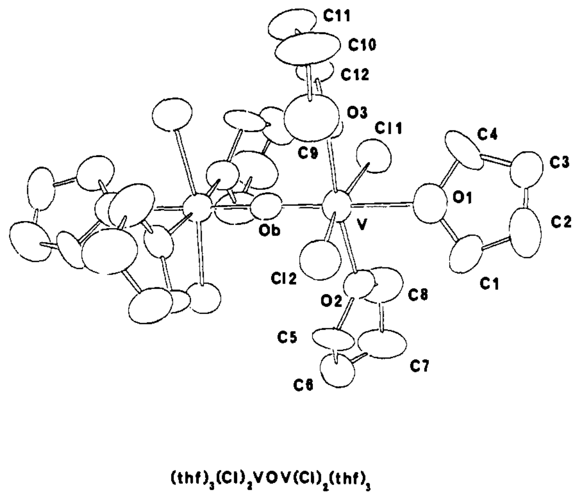

Figure 1. ORTEP drawing of the dimer $[(THF)_3Cl_2VOVCl_2(THF)_3]$ showing the labeling scheme.

It is to be noted that $VOCl_3–AlEt_3$[46] and $VCl_3–AlEt_3$ in *n*-heptane and $V(THF)_3Cl_3–(i\text{-}Bu)_3Al$[47] in *n*-hexane are proven Ziegler–Natta systems. A requirement for such a system is thought to be coordinative unsaturation on a reduced transition metal[48] (hence the use of hydrocarbon solvents of low coordinative ability). The $V–O_{THF}$ bond order in the title compound (ca. 0.6) and the consequent facile loss of solvent from the crystal lattice (see Experimental Section) are noteworthy in this respect. Since the presumed active homogeneous catalytic species, if mononuclear, would be VCl_2S_3R, where S is a solvent molecule easily displaceable by an olefin moiety and R is the ethyl group, the detrimental effect of oxidation appears to be dimer formation and consequent loss of stereochemical flexibility.

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Registry No. A, 92144-94-0; B, 92144-95-1; $ZnEt_2$, 557-20-0; VCl_3, 7718-98-1; $AlEt_3$, 97-93-8.

Supplementary Material Available: A stereoscopic view of the cell packing arrangement for $[(THF)_3Cl_2VOVCl_2(THF)_3]$ and tables of anisotropic thermal parameters (U_{ij}'s), selected nonbonded contacts, and calculated and observed structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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