the transfer of four electrons. CPE results confirm that four electrons per molecule are transferred at −1.1 V. There would appear to be only two possibilities for a four-electron process: (1) all four electrons are used to reduce Cu(II) to Cu(0) and no UO_2^{2+} electrochemistry is observed or (2) all four metal ions are reduced, yielding two Cu(I) and two U(V) centers. The quasi-reversibility of the CV wave argues strongly against the production of Cu(0) since formation of Cu(Hg) amalgam would preclude any significant degree of reversibility. Thus, one must conclude that the four electrons transferred ultimately reside on the four metals. Why the U(VI) → U(V) reduction potential should be shifted by +300 mV in $Cu_2(UO_2)_2(MOB)_2$ is not at all clear. Nor is it obvious why the reduction potentials of Cu(II) and UO_2^{2+} should be so similar in this compound. The unique feature of $Cu_2(UO_2)_2(MOB)_2$ compared to the others in the series is that the transition-metal ion (Cu^{2+}) reduces more positively than the UO_2^{2+} ions. It is possible that the formation of Cu^+ centers at −0.8 V produces geometric and electronic changes that facilitate the reduction of UO_2^{2+} and/or stabilize UO_2^+.

The compound $Cu_2(UO_2)_2(MOB)_2$ is of considerable interest since the observation of well-behaved four-electron-transfer electrochemistry is very rare. The tetranuclear Cu complex of MOB^{4-} also exhibits four-electron-transfer electrochemistry at essentially the same potential.[5] The CA and CPE results for the two compounds are very similar and consistent with the transfer of four electrons. However, the CV results for $Cu_2(UO_2)_2(MOB)_2$ show that the electron transfer is significantly more reversible in this molecule than in $Cu_4(MOB)_2$.

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Oxovanadium Alkoxides: Structure, Reactivity, and ^{51}V NMR Characteristics. Crystal and Molecular Structures of $VO(OCH_2CH_2Cl)_3$ and $VOCl_2(THF)_2H_2O$

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The vanadyl esters $VO(OR)_3$ (R = Me, Et, Pr, iPr, sBu, tBu, CH_2CH_2F, CH_2CH_2Cl, CH_2CCl_3) have been prepared and their association properties in pentane investigated by ^{51}V NMR. Limiting (low concentration) $\delta(^{51}V)$ values depend on the bulk of R (highest ^{51}V shielding for tBu). Shielding decreases with increasing concentration (more pronounced for small R groups), owing to the formation of oligomers, probably connected by μ-OR groups. The X-ray diffraction study of $VO(OCH_2CH_2Cl)_3$ (space group $P\bar{1}$; $a = 766.2$ (2) pm, $b = 907.5$ (4) pm, $c = 957.0$ (2) pm, $\alpha = 82.08$ (3)°, $\beta = 66.90$ (2)°, $\gamma = 79.42$ (3)°) reveals dimer association of molecules belonging to adjacent unit cells via long V–OR bonds (226.1 (2) pm), and a trigonal-bipyramidal geometry for each monomeric unit. From the reaction between $VOCl_3$ and diols (glycol, 1,3-propanediol, 1,2-, 2,3-, 1,3-, and 1,4-butanediol), complexes are obtained that contain the $\{VOCl(OR)_2\}$ and $\{VOCl_2OR\}$ moieties and the alcohol coordinated in the monofunctional or bifunctional (chelating and bridging) mode. The ^{51}V NMR spectrum of $VOCl_2OCH(Me)CH(Me)OH$ exhibits resolved ^{51}V–$^{35,37}Cl$ coupling: $J(^{51}V–^{35}Cl) = 100$ Hz; $J(^{51}V–^{37}Cl) = 83$ Hz. $V^VOCl_2(OCH_2CH_2CH_2CH_2OH)$ reacts with 1,4-butanediol to form $V^{IV}OCl_2(THF)_2(OH_2)$ (space group $C2/c$; $a = 1221.7$ (5) pm, $b = 1710.9$ (7) pm, $c = 922.3$ (4) pm, $\beta = 138.53$ (22)°). In the presence of $VOCl_3$, THF undergoes ether splitting, chlorination, and coordination to vanadium to yield $VOCl_2(OCH_2CH_2CH_2CH_2Cl)$.

Introduction

Metal alkoxides are valuable precursors for electronic and ceramic materials,[1] and volatile species, such as the alkoxides of V^{IV} and V^V, are potential candidates for chemical vapor deposition of metal and metal oxides. A more classical and nonetheless rapidly developing field of application for vanadium alkoxides and related compounds (e.g. complexes with ketols) is their use as catalysts in polymerization[2] and oxidation reactions.[3] Furthermore, interest has recently focused on vanadyl alkoxides $VO(OR)_{3-n}(OH)_n$ (esters of the hypothetic orthovanadic acid) as model compounds for the interaction of vanadate with the tyrosine and serine constituents of enzymes involved in phosphorylation reactions, which are commonly inhibited or stimulated by vanadate.[4] A V–OR bond has also been proposed for the coordination environment of V^V in vanadate-dependent haloperoxidase from a marine brown alga on the basis of an EXAFS study, which revealed one rather short V–O single bond.[4f]

In *aqueous* media, OH-functional molecules such as monoalcohols,[5a,b] diols,[5c,d] saccharides,[5d] nucleosides,[5e,6a] lactic acid,[5f]

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Table I. Structure Solution and Refinement

	1	**8**
cryst dimens, mm	0.5 × 0.3 × 0.1	0.2 × 0.3 × 0.25
no. of obsd reflcns	5350	1804
no. of significant reflcns ($\vert F_o\vert > 4\sigma(F_o)$)	4487	1414
scan range, deg	$4.5 < 2\theta < 70$	$4.5 < 2\theta < 50°$
no. of refined params	175	106
difference Fourier synthesis		
max e Å^3	0.64	0.60
min, e Å^3	−0.57	−0.85
R value $\sum\vert F_o - F_c\vert/\sum\vert F_o\vert)$	0.043	0.051
R_w value $(\sum w(\vert F_o - F_c\vert)^2/\sum w\vert F_o\vert^2)$	0.042	0.052

and citric acid[6b,c] form tetrahedral esters of composition $HVO_3(OR)^-$, $VO_3(OR)_2^-$, and $VO_2(OR)_2^-$. Esters derived from divanadic acid have also been reported. In addition, trigonal-bipyramidal and octahedral complexes exist. The former are of considerable interest in the context of transition-state analogues in the enzymatic formation and cleavage of phosphoester bonds.[4c] Formation constants for the vanadium compounds in water, although several orders of magnitudes larger than those for the esters of phosphoric acid, are still small (typically around 1 L/mol for a 1:1 complex[5]), and characterization of the respective compounds is restricted to systems containing a large excess of, e.g., an alcohol or a hydroxycarboxylate. Pursuing former work,[7,8] we have carried out investigations in non-aqueous media, where the triesters (tris(alkoxides)) $VO(OR)_3$ and mixed ester halides readily form.

Experimental Section

General and Spectroscopic Measurements. All operations were carried out under N_2 atmosphere to avoid hydrolysis and catalytic reduction of the extremely sensitive vanadyl esters and ester chlorides. Since V^V compounds are usually light-sensitive, direct sunlight was kept out during preparation and the products were stored in the dark. $VOCl_3$ (Aldrich) was distilled under N_2 and slightly reduced pressure. Monoalcohols were dried and purified by standard methods (MeOH and EtOH by reacting off the water with Mg shavings, and the other alcohols (neat or dissolved in chloroform), with molecular sieve (3 Å). Diols, dissolved in $CHCl_3$, were dried on Al_2O_3. Where necessary, the chloroform was removed by distillation. The purified alcohols were kept under N_2.

IR spectra were obtained for the neat samples (if oils) or in KBr pellets on Perkin-Elmer spectrometers (Models 577 and 325) and were employed mainly to characterize the compounds with respect to the degree of alkoxylation: IR for $VOCl_{3-n}(OR)_n$: for $n = 1$, $\nu(V{=}O) = 1025–1028\ cm^{-1}$, $\nu(VCl) = 490–499\ cm^{-1}$; for $n = 2$, $\nu(V{=}O) = 1014–1017\ cm^{-1}$, $\nu(VCl) = 460–480\ cm^{-1}$; for $n = 3$, $\nu(V{=}O) = 1005–1008\ cm^{-1}$. No obvious relation seems to exist between the stretching frequencies and the degree of association.

^1H and $^{13}C\{^1H\}$ NMR: Bruker WP 80 instrument, employing the usual measuring parameters. $^{51}V\{^1H\}$ NMR: (1) Bruker AM 360 instrument, 94.6 MHz, pulse angle 40°, relaxation delay 1 s, sweep width 100 kHz, time domain 4 K, 4K zero filling; (2) Bruker WP 80 instrument, using a selective ^{13}C probe head (measuring frequency 21.04 MHz), pulse angle 60°, relaxation delay 1 s, sweep width 125 kHz, time domain 8 K, 8K zero filling. All ^{51}V NMR measurements were carried out in rotating 10-mm vials at 298 (2) K; $\delta(^{51}V)$ values are quoted relative to $VOCl_3$. Paramagnetic impurities, present in solution in same cases, do not influence the $\delta(^{51}V)$ values beyond the experimental error (ca. ±1 ppm). They do influence relaxation, however, and hence line widths. The resonance of a V^V species is still detectable at a reasonable signal-to-noise if the V^{IV} impurity does not exceed ca. 1% of the overall vanadium contents. Depending on the width of the resonance line, the detection level for V^V, under the measuring conditions noted above, is 10 to 2 mmol/L. With the overall concentrations usually maintained for purity checks (250 mmol/L), V^V byproducts of more than 0.05–1% show up in the ^{51}V NMR. The V^{IV} species are undetectable by ^{51}V NMR.

X-ray Structures. Data were collected on a Syntex P2$_1$ diffractometer at room temperature in the $\theta/2\theta$ scan mode using a graphite monochromator and Mo Kα radiation. The structures were solved by the use of the program systems SHELXS-86,[9] PATSEE,[10] and MITHRIL,[11] and refined with SHELX-76.[12] Absorption corrections have not been carried out. For further experimental details, see Table I. The positions of the hydrogen atoms were obtained from a Fourier difference synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically.

Preparation of Compounds. Oxovanadium Alkoxides $VO(OR)_3$ Derived from Monoalcohols. The preparation in part follows a procedure described earlier:[13] 3–5 g of finely pulverized V_2O_5 was treated with a 10-fold molar excess of the alcohol and benzene (*n*-pentane for R = Me) and heated to the boiling point. Reaction water was distilled off as an azeotrope and collected in a water trap to control the propagation of the reaction. After water separation had ceased, decomposition products were filtered off, and excess benzene and alcohol were removed in vacuo. In the case of R = Et, nPr, iPr, sBu, and tBu, the pure tris(alkoxides) were obtained by fractional distillation under high vacuum. For the new compounds with R = CH_2CH_2Cl, CH_2CH_2F, and CH_2CCl_3, purification was carried out by recrystallization from *n*-pentane.

Yields vary from 67% to 73% for the purified products. $VO(OCH_2CH_2Cl)_3$ (**1**): Yield = 73%. Anal. Calcd for $C_6H_{12}Cl_3O_4V$: C, 23.59; H, 3.96; Cl, 34.82; V, 16.68. Found: C, 23.6; H, 3.85; Cl, 35.1; V, 16.6. For the raw materials, yields (80–90%) are higher if R is a bulky substituent and/or carries Cl or F. The main loss of material occurs during distillation, mainly through thermal decomposition, and is more pronounced for esters with bulky R groups. The purity of all complexes was measured by ^{51}V NMR (cf. Table IV for data). The concentration dependence of $\delta(^{51}V)$ in pentane was determined at 298 K and 21.04 MHz. Crystals of **1** were obtained by allowing a saturated solution in pentane to stand for 2 months at 277 K.

Alkoxooxochlorovanadium Complexes Derived from Diols. Preparation of Lithium Alcoholates. The diol was dissolved in $CHCl_3$ and dried dynamically with aluminum oxide (90 active, basic, activity I; Merck). The chloroform was distilled off, and the dry diol was dissolved or suspended in pentane and treated dropwise with a hexane solution of LiBu (1.6 M; Merck). A molar ratio diol/LiBu = 1/1 or 1/2 was employed to prepare the mono- or dilithium salts. The lithium alcoholates were filtered off, washed several times with pentane and finally with $CHCl_3$, and dried in vacuo.

$\overline{\mathrm{VOCl(OCH_2CH_2O}}\mathrm{)}$ (2). A 0.79-g (31.8-mmol) sample of dilithium glycolate was suspended in 20 mL of *n*-pentane and treated, at room temperature, with a solution of 1.85 g (10.7 mmol) of $VOCl_3$ in 10 mL of pentane. The mixture was refluxed for 30 min and filtered, and the filtrate was evaporated to dryness. The residue was redissolved in CH_2Cl_2, filtered, and concentrated. **2** precipitated in the form of a light yellow, microcrystalline powder. This was filtered off and dried in high vacuum. Yield = 65%. Anal. Calcd for $C_2H_4ClO_3V$: C, 14.79; H, 2.48; V, 31.36. Found: C, 15.1; H, 2.86; V, 31.2. ^{51}V NMR: δ −438 ppm. ^1H NMR: δ 5.3 and 5.9 ppm. The resonances are broad and shifted to low field by 3.7 ppm with respect to that for free glycol.

$\overline{\mathrm{VOCl(OCH_2CHO}}\mathrm{CH_2CH_3)}$ (3a) and $\{VOCl_2\}_2\{\mu\text{-}OCH_2CH(CH_2CH_3)O\}$ (3b). **3a**: A 4.5-g (44.1-mmol) sample of dilithium 1,2-butanediolate, suspended in 40 mL of CH_2Cl_2, was treated dropwise with 10 mL of a pentane solution containing 1.7 g (10.0 mmol) of $VOCl_3$. After being stirred for 2 days at room temperature, the reaction mixture was filtered and the filtrate evaporated to dryness. **3a** was isolated as a viscous, dark red oil. ^{51}V NMR: δ −462 ppm. **3b**: A 2.5-g (24.5-mmol) sample of dilithium 1,2-butanediolate and 4.2 g (24.5 mmol) of $VOCl_3$ were reacted analogously to produce a dark red, viscous oil, **3b**. ^{51}V NMR: δ −282 and −298 ppm. ^1H NMR: δ 5.9 ppm (3 H, broad, C1H_2 plus C2H). ^{13}C NMR: δ 93 (C1) and 103 (C2) ppm, broad.

$VOCl_2OCH(CH_3)CH(CH_3)OH$ (4a). A 2.58-g (26.9-mmol) sample of the monolithium salt of 2,3-butanediol was suspended in 40 mL of CH_2Cl_2 and treated with a solution of 6.6 g (37.9 mmol) of $VOCl_3$ in 20 mL of pentane. After the mixture was stirred at room temperature for 2 days, followed by filtration and evaporation to dryness, **4a** was isolated as a red oil. ^{51}V NMR: δ −294 ppm, "quintet" (cf. Figure 5), $J(^{51}V–^{37}Cl) = 83$ Hz, $J(^{51}V–^{35}Cl) = 100$ Hz. If a solution of **4a** is allowed to stand for several days, HCl evolves and a second ^{51}V resonance (−480 ppm) arises, which represents a compound of general composition $VOCl(OR)_2$ (**4b**).

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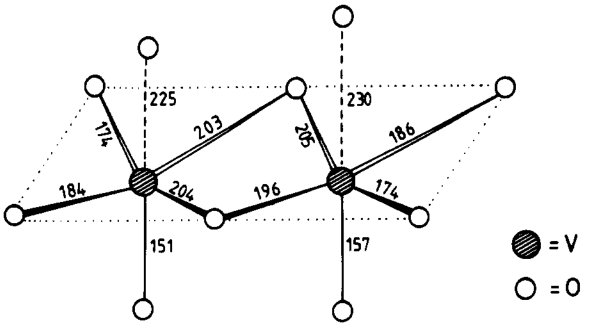

Figure 1. Structure of $VO(OMe)_3$, showing its dimeric nature in the solid state. Redrawn from ref 23. Bond lengths in pm.

$VOCl(OCH_2CH_2CH_2OH)_2$ (5). A 2.0-g (24.5-mmol) sample of $LiOCH_2CH_2CH_2OH$ was suspended in 30 mL of pentane, 1.42 g (8.2 mmol) of $VOCl_3$ dissolved in 20 mL of pentane was added dropwise, and the solution was stirred at room temperature for 30 min. The filtrate from this reaction mixture was evaporated to dryness, the dark gray residue redissolved in CH_2Cl_2, the solution filtered, and the solvent removed in vacuo to yield yellow-brown **5**. Yield: 70%. Anal. Calcd for $C_6H_{14}ClO_5V$: C, 28.53; H, 5.59; V, 20.17. Found: C, 28.9; H, 5.45; V, 20.1. ^{51}V NMR: δ −429 ppm.

$HOCH(CH_3)CH_2CH_2OVOCl\{\mu\text{-}OCH(CH_3)CH_2CH_2O\}VO(OCH_2CH(CH_3)CH_2O)$ (6). A 4.3-g (24.8-mmol) sample of $VOCl_3$ dissolved in 10 mL of pentane was added to 3.0 g of a 1:1 mixture of the mono- and dilithium salts of 1,3-butanediol in 30 mL of CH_2Cl_2 and stirred for 2 days at room temperature. After filtration and evaporation, **6** was obtained as a yellow-brown, viscous oil. ^{51}V NMR: δ −429 and −562 ppm. Anal. Calcd for $C_{12}H_{25}ClO_8V_2$: C, 33.16; H, 5.80; V, 23.44. Found: C, 33.3; H, 5.67; V, 23.1.

Reaction between $VOCl_3$ and 1,4-Butanediol To Give 7 and 8. A 5.0-g (55.5-mmol) sample of well-dried, 1,4-butanediol was dissolved in 20 mL of pentane and treated, at room temperature, with 4.7 g (27.5 mmol) of $VOCl_3$ in 10 mL of pentane. A red solution containing $VOCl_2(OCH_2CH_2CH_2CH_2OH)$ (**7**) (^{51}V NMR: δ −290 ppm) was obtained. After being allowed to stand overnight, the solution had turned blue by formation of a VO^{2+} complex. Crystals of $VOCl_2(OCH_2CH_2CH_2CH_2)_2(H_2O)$ (**8**) grew from this solution within several days at room temperature. Yield = 63%. Anal. Calcd for $C_8H_{18}Cl_2O_4V$: C, 32.02; H, 6.05; Cl, 23.63; V, 16.98. Found: C, 31.8; H, 6.03; Cl, 23.8; V, 16.8.

Results and Discussion

Esters of Monoalcohols. General Data. Simple vanadyl esters and mixed ester chlorides $VOCl_{3-n}(OR)_n$ have been known for about 80 years[14] and studied thouroughly in several of their aspects, including ^1H[13] and ^{51}V NMR properties[7] and IR,[15,16] mass spectrometric,[16,17] and thermolytic characteristics.[18] The mixed ester chlorides are obtained from $VOCl_3$ and $VO(OR)_3$[19a] or by direct reaction of $VOCl_3$ with alcohols in inert solvents such as pentane or CH_2Cl_2. If NH_3 is used as a scavenger for HCl, the triesters are isolated;[19] they can also be prepared by using the sodium or lithium alcoholates.[14] The use of alcoholates instead of alcohols is advantageous because of the greater resistance of the former toward oxidation. An alternative route, preferably for the generation of $VO(OR)_3$ with bulky substituents R, is transesterification[19a,20] or the reaction between V_2O_5 and the alcohol with the removal of reaction water by azeotropic distillation[13] or with molecular sieves. The pure triesters are colorless. Traces of moisture give rise to the formation of the yellow esters of hexavanadic acid, $V_6O_{13}(OR)_4$. With larger amounts of water, complete hydrolysis to colloidal red V_2O_5 takes place.[14]

Table II. Fractional Coordinates and Isotropic Thermal Factors for $VO(OCH_2CH_2Cl)_3$ (**1**)

atom	x/a	y/b	z/c	U_{eq}, Å^2
V	0.0672 (1)	0.6707 (1)	0.9778 (1)	0.034 (1)
O	−0.0087 (2)	0.8207 (2)	1.0637 (2)	0.045 (1)
O_1	−0.1179 (2)	0.5578 (2)	1.1117 (1)	0.036 (1)
C11	−0.2492 (3)	0.5977 (3)	1.2607 (2)	0.042 (2)
C12	−0.1406 (4)	0.5812 (3)	1.3647 (2)	0.050 (2)
Cl1	−0.3016 (1)	0.6405 (1)	1.5479 (1)	0.072 (1)
O2	0.0663 (2)	0.7347 (2)	0.7948 (2)	0.046 (1)
C21	0.0399 (4)	0.8832 (3)	0.7299 (3)	0.053 (2)
C22	0.2061 (5)	0.9095 (3)	0.5849 (3)	0.060 (3)
Cl2	0.2221 (1)	0.7974 (1)	0.4412 (1)	0.073 (1)
O3	0.2961 (2)	0.6210 (2)	0.9873 (2)	0.047 (1)
C31	0.3881 (4)	0.6928 (3)	1.0564 (3)	0.053 (2)
C32	0.5527 (4)	0.7628 (3)	0.9420 (3)	0.058 (2)
Cl3	0.4747 (1)	0.9178 (1)	0.8346 (1)	0.076 (1)
H11	−0.3129 (34)	0.7025 (27)	1.2536 (26)	0.047 (6)
H11	−0.3505 (33)	0.5293 (26)	1.2987 (26)	0.043 (6)
H12	−0.0817 (39)	0.4877 (32)	1.3738 (30)	0.059 (8)
H12	−0.0446 (36)	0.6474 (28)	1.3364 (28)	0.049 (7)
H21	−0.0752 (40)	0.8943 (30)	0.7082 (31)	0.059 (8)
H21	0.0258 (41)	0.9655 (33)	0.7993 (33)	0.072 (9)
H22	0.1940 (40)	1.0135 (34)	0.5546 (32)	0.066 (8)
H22	0.3203 (42)	0.8830 (32)	0.5961 (32)	0.066 (9)
H31	0.4355 (40)	0.6156 (32)	1.1158 (32)	0.067 (8)
H31	0.2984 (38)	0.7714 (30)	1.1151 (30)	0.057 (7)
H32	0.6152 (36)	0.8084 (29)	0.9886 (29)	0.054 (7)
H32	0.6376 (42)	0.6837 (34)	0.8743 (34)	0.075 (9)

Table III. Selected Bond Distances (pm) and Angles (deg) of **1**

	Bond Distances		
V–O	158.4 (2)	O···O′	259.7 (2)
V–O1	185.7 (1)	O···O2	260.6 (2)
V–O2	177.1 (2)	O···O3	259.7 (2)
V–O3	176.3 (2)	O1···O2	314.7 (2)
V–O1′	226.1 (2)	O1···O3	305.3 (2)
V···V′	336.1 (1)	O2···O3	298.6 (3)
V···O′	226.1 (2)		
	Bond Angles		
O3–V–O1′	85.82 (9)	O–V–O3	101.62 (11)
O2–V–O1′	82.76 (7)	O–V–O2	101.81 (9)
O2–V–O3	115.31 (9)	O–V–O1	97.57 (8)
O1–V–O1′	70.97 (7)	V–O1–V′	109.03 (7)
O1–V–O3	114.97 (8)	V–O1–C11	125.33 (16)
O1–V–O2	120.30 (9)	V–O2–C21	130.01 (16)
O–V–O1′	168.30 (9)	V–O3–C31	129.80 (18)

Molecular Association. Cryoscopic measurements,[21] mass spectrometric investigations,[17] and preliminary ^{51}V NMR studies[7b,22] have revealed that there is a tendency for the molecules $VO(OR)_3$ to form, in solution, dimers and oligomers. The extent of cluster formation has been shown to depend on temperature, solvent, concentration, and size of R.[13,21] Dimer formation has been backed up by an early X-ray structure analysis of $VO(OMe)_3$,[23] the only simple alkyl ester that is solid at room temperature. The compound forms *dimeric* units (Figure 1), linked symmetrically by alkoxide oxygens, and exhibits a tetragonal-pyramidal arrangement in each half of the dimer. A sixth coordination site is occupied by a relatively weakly bound alkoxide oxygen of a neighboring dimer.

We have now determined the crystal and molecular structure of $VO(OCH_2CH_2Cl)_3$ (**1**), the second example of a vanadyl alkyl ester structurally characterized in the crystalline solid state. **1** crystallizes in the triclinic space group $P\bar{1}$.[24] Fractional coordinates and isotropic thermal factors are given in Table II, and

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(16) Turevskaya, E. P.; Kozlova, N. I.; Turova, N. Ya.; Kessler, V. G. *Koord. Khim.* **1988**, *14*, 926.

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(24) $C_6H_{12}Cl_3O_4V$, M_r = 305.46 g/mol; a = 766.2 (2) pm, b = 907.5 (4) pm, c = 957.0 (2) pm, α = 82.08 (3)°, β = 66.90 (2)°, γ = 79.42 (3)°, V = 600.11 × 10^6 pm^3, Z = 2, ϱ(calcd) = 1.69 kg/L, μ = 14 cm^{-1}.

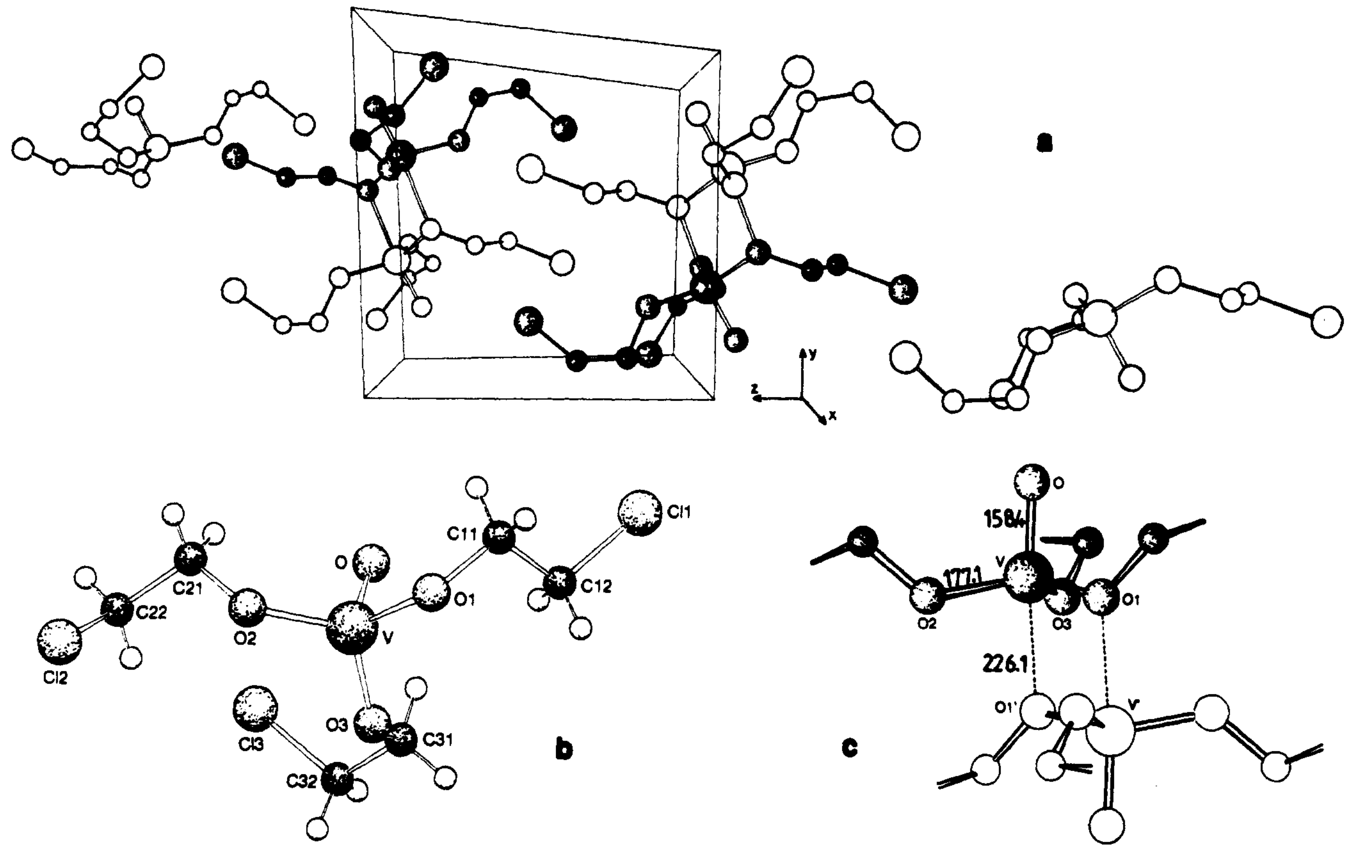

Figure 2. Graphical representation of $VO(OCH_2CH_2Cl)_3$: (a) unit cell (shaded molecules) and molecules from neighboring unit cells; (b) numbering scheme and view of the monomer; (c) Section of the unit cell, showing the "dimers" formed by intermolecular contacts between two symmetry-related molecules of adjacent unit cells. Bond lengths are given in pm.

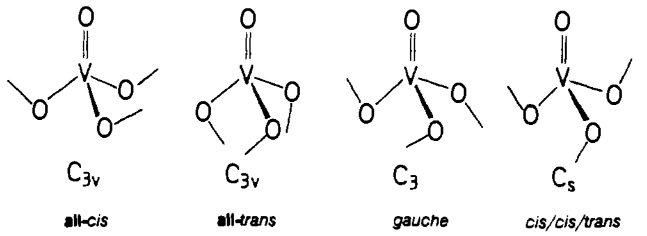

Figure 3. Possible rotamers for $VO(OR)_3$. The all-cis, cis/cis/trans, and gauche isomers have been found for R = tBu by vibrational analysis.[15] For R = CH_2CH_2Cl in the crystalline state, the all-cis isomer is realized.

selected bonding parameters are given in Table III. The unit cell and the structure of the molecule are illustrated in Figure 2. **1** is *monomeric*, and in a flat trigonal-pyramidal array, with the vanadium atom 30 pm out of the plane of the three alkoxide oxygens. The alkyl substituents are in the all-cis configuration, thus providing local C_{3v} symmetry (Figure 3). This isomer has been shown (by Raman and IR spectroscopy[15]) to be present in solutions of $VO(OtBu)_3$ together with two other rotamers with the alkyls in the gauche (C_3) and cis/trans positions (C_s) (Figure 3). The slightly less stable (by 0.8 kJ/mol) C_{3v} isomer is the preferred one in the case of compound **1**, where it allows for a loose association of the molecules in the solid: two symmetry-related molecules of neighbouring unit cells are in intermolecular contact (Figure 2c), providing a trigonal-bipyramidal environment for vanadium, an interesting point in view of the postulated transition state for enzymatic phosphoester formation and hydrolysis mentioned in the Introduction. Intermolecular bond distances V–O1' (V'–O1) are 226.1 (2) pm, which compares to the *inter*molecular contacts in $[VO(OMe)_3]_2$ (225 and 230 pm; Figure 1) and long *intra*molecular V–O distances in clusters such as $V_6O_6(\mu\text{-}O)_4(O_2CPh)_9$[25] or $V_3O_3(O_2CPh)_6(THF)$.[26] In partial agreement with earlier investigations by ^1H NMR[13] and also in agreement with a ^{51}V NMR study on the dimer $[V_2O_2(OiPr)_7]^-$,[22] the "bridging" oxygens in **1** are those carrying the alkyl groups.

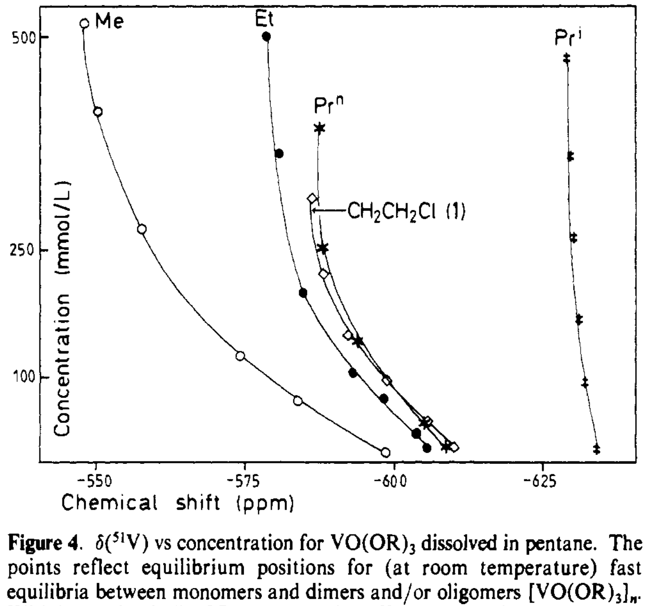

Figure 4. $\delta(^{51}V)$ vs concentration for $VO(OR)_3$ dissolved in pentane. The points reflect equilibrium positions for (at room temperature) fast equilibria between monomers and dimers and/or oligomers $[VO(OR)_3]_n$. With increasing bulk of R, concentration effects become less pronounced. $VO(tBu)_3$ does not associate.

The tendency of vanadyl esters to associate is also reflected by their solution ^{51}V NMR patterns (Table IV and Figure 4). We have shown earlier that ^{51}V NMR spectroscopy is a sensitive tool in the investigation of exchange processes between monomers and oligomers in solution.[7b] ^{51}V shielding depends on electronic *and steric* factors. Crowding around the vanadium center leads to

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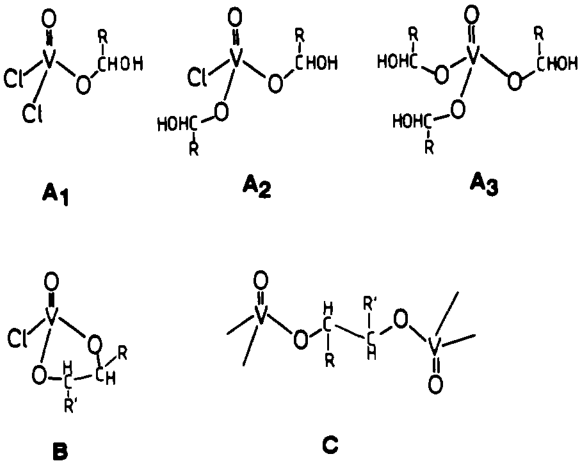
Table IV. Limiting (Low and High Concentration) $\delta(^{51}V)$ Values and Oligomerization Shifts $\Delta\delta$ for Vanadyl Alkoxides $VO(OR)_3$ in *n*-Pentane

R	$\delta(^{51}V)$,[a] ppm		$\Delta\delta$,[b] ppm L/mol	concn range, mmol/L
CH_2CH_2F	−595	*c*	*c*	100
CH_3	−598.2	−547.5	99	12–520
$CH(Me)CH_2CH_3$	−600	*c*	*c*	100
$CH_2CH_2CH_3$	−603.7	−587.2	33	12–390
CH_2CH_3	−605.4	−573.0	57	19–770
CH_2CH_2Cl	−608.6	−585.8	54	18–310
CH_2CCl_3	−628	*c*	*c*	100
$CHMe_2$	−634.5	−627.7	13	10–480
CMe_3	−681.4	−681.0	1	0.5–460

[a] Relative to $VOCl_3$. The first entry is for low concentration; the second is for high concentration. [b] δ(high concn) − δ(low concn), determined at room temperature for the concentration range indicated and extrapolated for an overall concentration gradient of 1 mol/L. [c] Not determined.

Scheme I



additional shielding as has been documented for vanadyl esters in aqueous[5a] and nonaqueous solutions[7a,c,d] and for the octahedral alkoxo compound $VO(oxine)_2OR$.[8] An increase of the coordination number, on the other hand, e.g., on going from tetrahedral to trigonal-bipyramidal or octahedral arrangements, is usually accompanied by a *de*crease of shielding.[5c-f,22,27] Both trends are illustrated in Figure 4: There is an increase of ^{51}V shielding as the bulk of the alkyl substituent increases, and there is a decrease of shielding as the equilibrium $nVO(OR)_3 \rightleftharpoons [VO(OR)_3]_n$ is shifted toward the *oligomer* with growing concentration (at least two oligomers differing in the degree of oligomerization are probably present[7b,c]). The oligomerization shift is particularly large for $VO(OMe)_3$ ($\Delta\delta$ = 99 ppm L/mol), and less pronounced for esters with sterically demanding R, which are less capable to form associates (cf. Table IV for data).

Esters of Diols. Preparation and Characteristics. The direct reaction between $VOCl_3$ and diols in inert solvents leads to the same reaction products that are obtained with monoalcohols, namely $VOCl_2\{OR\}$ and $VOCl\{OR\}_2$. $\{OR\}$ stands for diolate(1−); $\{OR\}_2$ stands for diolate(2−) or $2\{OR\}$. The pattern of reactants is more complex, however, since, depending on the reaction conditions and the nature of the diol, three principal types of compounds may form, A, B, and C in Scheme I. The formation of the chelates B is favored with diols containing vicinal OH groups and in 1:1 mixtures with $VOCl_3$. Bridged species C can be expected with an excess of $VOCl_3$ and diols with more distant or sterically hindered alcoholic functions. To achieve removal of a third chlorine and hence to generate $VO\{OR\}_3$ (A_3) type compounds, monolithium and dilithium alkoxides have to be employed. Again, the use of lithium salts instead of the alcohols themselves stabilizes the systems against redox reactions. In Table V, results are collated; for assignment (on the basis of ^{51}V data), a few mixed chloride esters of monoalcohols have been added.

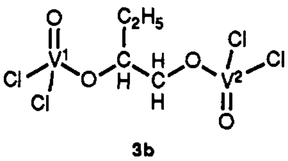
Table V. Vanadyl Alkoxides Derived from Butanols and Various Diols

diol[a]	compd	type[b]	$\delta(^{51}V)$[c]	comments[a,d]
1-butanol		A_1	−290	
		A_2	−470	
2-butanol		A_1	−288	
		A_2	−478	
glycol	**2**	B	−438	the CH_2s are inequivalent[e]
1,2-butanediol	**3a**	B	−462	with excess of the Li_2 salt
	3b	$C(A_1)_2$	−282; −298[f]	molar ratio of reactants 1/1
2,3-butanediol	**4a**	A_1	−294	coupling to $^{35/37}Cl$ resolved
	4b	B/CA_1A_2	−480	by spontaneous HCl elimination[g]
1,3-propanediol	**5**	A_2	−429	ν_{OH} = 3200–3600 cm^{-1}
1,3-butanediol	**6**	CA_2A_3	−429; −562[h]	tentative formulation
1,4-butanediol	**7**	A_1	−290	converts to $VOCl_2(THF)_2$-(H_2O)

[a] For the reaction conditions and further details (spectroscopic parameters), see the Experimental Section. [b] Cf. Scheme I. [c] Relative to $VOCl_3$. [d] Cf. text for discussion. [e] The inequivalence may reflect differing arrangements of the two OR groups (e.g. cis and gauche) as shown in Figure 3. [f] Equal integral intensities. [g] After 10 days, the ratio of the species giving rise to the −294 and −480 ppm signals is 4/1 (by ^{51}V NMR). [h] Integral intensities 1 and 1.1.

^{51}V NMR again proves a powerful tool: it allows for an unambiguous decision on the number of chlorines still bound to vanadium. There are distinct shift ranges for $VOCl_2\{OR\}$, $VOCl\{OR\}_2$, and $VO\{OR\}_3$ (for the latter see Table IV), and this is a consequence of the dependence of ^{51}V shielding on *electronic* factors discussed in detail elsewhere.[27,28] In our case, the inverse dependence of shielding in these d^0 complexes on the ligand electronegativity leads to a high-field (low-frequency) shift of the resonance by ca. 200 ppm per exchange of Cl by OR.[7d]

Simple A_1 or A_2 type complexes are formed with the diols or the monolithium salts. In the latter case, OH groups remain dangling (as evidenced by IR) and may slowly react, within days to months, to form more complex compounds by inter- or intramolecular HCl elimination. This is the case for **4a**, which converts to a mononuclear chelate complex (B) or a dinuclear, bridged complex with two inequivalent V centres (CA_1A_2). **7** is unstable toward internal redox processes and is discussed in more detail in the next section. A reaction to form type B complexes takes place if $VOCl_3$ is reacted with the dilithium salts of ethylene glycol or 1,2-butanediol to generate **2** and **3a**. Changing the reaction conditions with 1,2-butanediol yields a second complex, **3b**, with two $VOCl_2$ moieties bridged by the diolate(2−):



3b

There are two ^{51}V NMR signals for **3b**. The one to slightly higher field (−298 ppm) is assigned to V^1, coordinated to the sterically more demanding *secondary* alcoholic group, for reasons discussed in the preceding section. Compound **4a** is of special interest from

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[27] Rehder, D.; Weidemann, C.; Duch, A.; Priebsch, W. *Inorg. Chem.* **1988**, *27*, 584.

[28] (a) Rehder, D. *Magn. Reson. Rev.* **1984**, *9*, 125. (b) Rehder, D. In *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987, Chapter 19. (c) Mason, J. *Chem. Rev.* **1987**, *87*, 1299. (d) Mason, J. *Polyhedron* **1989**, *13/14*, 1657.

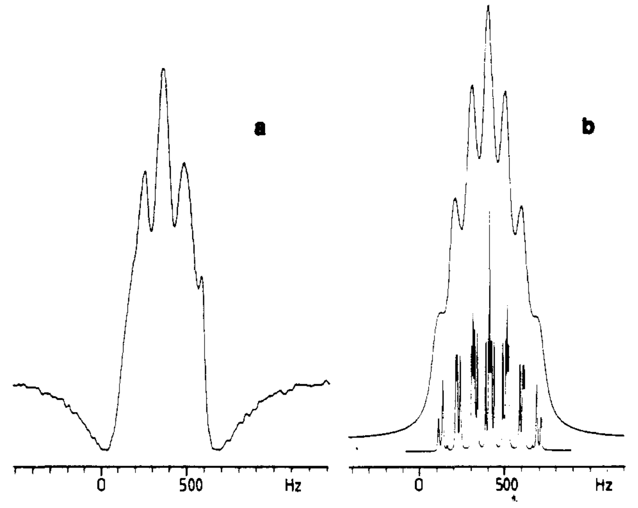

Figure 5. Experimental (a) and simulated (b) 21.03-MHz ^{51}V NMR spectra of $VOCl_2\{OCH(Me)CH_2(OH)Me\}$ (**4a**). Simulations have been carried out for the following isotopomeric composition: 57% $^{51}V(^{35}Cl)_2$, 37% $^{51}V^{35}Cl^{37}Cl$, and 6% $^{51}V(^{37}Cl)_2$ (the isotope ^{50}V (natural abundance 0.24%) has not been considered), with widths of the resonance lines at half-height of 80 (b) and 1 Hz (inset).

Table VI. Fractional Coordinates and Isotropic Thermal Factors for $VOCl_2(THF)_2(H_2O)$ (**8**)

atom	x/a	y/b	z/c	U_{eq}, Å^2
V	0.0000 (0)	0.1174 (1)	0.2500 (0)	0.038 (1)
O1	0.0000 (0)	0.0248 (2)	0.2500 (0)	0.056 (4)
O2	0.0000 (0)	0.2482 (2)	0.2500 (0)	0.062 (5)
Cl1	−0.2375 (1)	0.1363 (1)	−0.1377 (2)	0.047 (1)
Cl1′	0.2375 (1)	0.1363 (1)	0.6377 (2)	0.047 (1)
O3	0.1577 (3)	0.1279 (2)	0.2305 (5)	0.050 (3)
O3′	−0.1577 (3)	0.1279 (2)	0.2695 (5)	0.050 (3)
C1	0.1268 (7)	0.1647 (4)	0.0603 (10)	0.071 (6)
C1′	−0.1268 (7)	0.1647 (4)	0.4397 (10)	0.071 (6)
C2	0.2795 (8)	0.1549 (4)	0.1279 (12)	0.089 (7)
C2′	−0.2795 (8)	0.1549 (4)	0.3721 (12)	0.089 (7)
C3	0.3584 (7)	0.0820 (3)	0.2627 (10)	0.071 (6)
C3′	−0.3584 (7)	0.0820 (3)	0.2373 (10)	0.071 (6)
C4	0.2921 (7)	0.0704 (3)	0.3445 (10)	0.074 (6)
C4′	−0.2921 (7)	0.0704 (3)	0.1555 (10)	0.074 (6)
H0	−0.0929 (60)	0.2725 (30)	0.1791 (88)	0.084 (18)
H0′	0.0929 (60)	0.2725 (30)	0.3209 (88)	0.084 (18)
H1	0.0563 (68)	0.2167 (32)	0.0064 (89)	0.083 (17)
H1′	−0.0563 (68)	0.2167 (32)	0.4935 (89)	0.083 (17)
H1	0.0359 (69)	0.1380 (33)	−0.0655 (90)	0.085 (19)
H1′	−0.0359 (69)	0.1380 (33)	0.5655 (90)	0.085 (19)
H2	0.2602 (66)	0.1533 (30)	0.0024 (93)	0.081 (17)
H2′	−0.2602 (66)	0.1533 (30)	0.4976 (93)	0.081 (17)
H2	0.3426 (152)	0.2097 (74)	0.2197 (199)	0.287 (63)
H2′	−0.3426 (152)	0.2097 (74)	0.2803 (199)	0.287 (63)
H3	0.4709 (74)	0.0801 (34)	0.3721 (97)	0.095 (20)
H3′	−0.4709 (74)	0.0801 (34)	0.1279 (97)	0.095 (20)
H3	0.2904 (87)	0.0316 (42)	0.1040 (116)	0.155 (28)
H3′	−0.2904 (87)	0.0316 (42)	0.3960 (116)	0.155 (28)
H4	0.3013 (81)	0.0480 (40)	0.4463 (109)	0.109 (23)
H4′	−0.3013 (81)	0.0480 (40)	0.0537 (109)	0.109 (23)
H4	0.2398 (67)	0.0107 (34)	0.2982 (93)	0.089 (18)
H4′	−0.2398 (67)	0.0107 (34)	0.2018 (93)	0.089 (18)

an NMR spectroscopic point of view since, to our knowledge, this is the first example where coupling of the chlorine nuclei (^{35}Cl, natural abundance 75.4%, nuclear spin $^3/_2$; ^{37}Cl, 24.6%, $^3/_2$) to a transition-metal nucleus, here ^{51}V (99.76%, $^7/_2$), is observed. The spectrum is shown in Figure 5. Its simulation leads to the one-bond coupling constants $^1J(^{35}Cl-^{51}V) = 100$ Hz and $^1J(^{37}Cl-^{51}V) = 83$ Hz. The reduced coupling constants are the same size within the limits of error.

Table VII. Selected Bond Distances (pm) and Angles (deg) for **8**

	Bond Distances		
V–O1	158.4 (4)	O3–C4	147.7 (9)
V–O2	223.7 (4)	C1–C2	146.8 (16)
V–Cl	240.0 (11)	C2–C3	149.5 (9)
V–O3	207.3 (10)	O2–H0	88.2 (6)
O3–C1	145.4 (10)		
	Bond Angles		
O1–V–O2	180.00 (49)	Cl–V–O3	91.36 (28)
O3–V–O3′	170.06 (15)	Cl–V–Cl′	64.52 (12)
O1–V–O3	94.97 (41)	O2–V–Cl	82.26 (13)
O2–V–O3	85.03 (32)	O1–V–Cl	97.74 (15)
Cl–V–O3′	87.30 (28)		

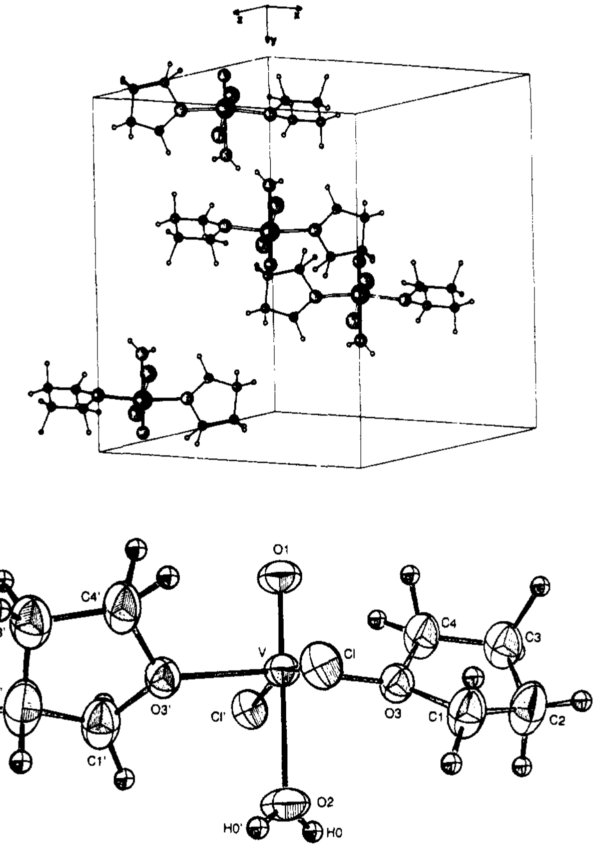

Figure 6. SCHAKAL representation of the unit cell and ORTEP plot with numbering scheme of an isolated molecule of $VOCl_2(THF)_2(H_2O)$ (**8**).

Reactions. As already mentioned above, the mixed ester chlorides formed by reaction between $VOCl_3$ and diols in solvents such as pentane may undergo redox processes. The red solution initially obtained with 1,4-butanediol containing, according to the $\delta(^{51}V)$ value (−290 ppm), $VOCl_2OR$ (**7**), shows the typically blue color of V^{IV} after standing for two days. From this solution, $VOCl_2(THF)_2(H_2O)$ (**8**) crystallizes. Water catalyzes the reduction of VO^{3+} to VO^{2+} in the presence of organic substrates. The primary step therefore should be a condensation reaction involving the intermediate 7, followed by reduction of vanadium. The overall reaction may be formulated in the following way:

$$VOCl_3 + HO(CH_2)_4OH \rightarrow \underset{\mathbf{7}}{VOCl_2O(CH_2)_4OH} + HCl \quad (1)$$

$$\underset{\mathbf{7}}{V^VOCl_2O(CH_2)_4OH} + HO(CH_2)_4OH + H^+ + e^- \rightarrow \underset{\mathbf{8}}{V^{IV}OCl_2(THF)_2(H_2O)} + H_2O \quad (2)$$

8 crystallizes in the monoclinic space group $C2/c$.[29] Fractional coordinates, thermal factors, and selected bonding parameters are contained in Tables VI and VII; drawings of the unit cell and the molecule are represented in Figure 6. The coordination geometry of **8** is almost ideally octahedral with V, the vanadyl and water oxygens, and the two Cls (in trans positions) forming a plane of

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(29) $C_8H_{18}Cl_2O_4V$, $M_r = 300.08$ g/mol; $a = 1221.7$ (5) pm, $b = 1710.9$ (7) pm, $c = 922.3$ (4) pm, $\beta = 138.53$ (22)°, $V = 1276.61 \times 10^6$ pm^3, Q(calcd) = 1.56 kg/L, $\mu = 11$ cm^{-1}.

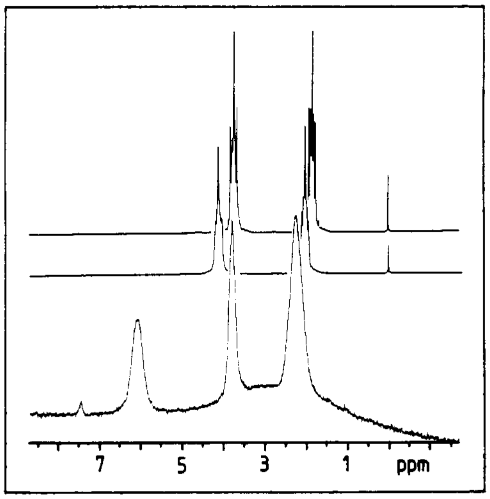

Figure 7. 80.1-MHz ^{1}H NMR spectra of THF (top), 1/1 THF/$VOCl_3$ (=$VOCl_3(THF)_n \rightleftharpoons VOCl_3 + n$THF; center), and 1/1 THF/$VOCl_3$ after a reaction time of two weeks (= **9**; bottom). All spectra were recorded in $CDCl_3$ solution and at 300 K.

the octahedron. V and the two THF oxygens are on a crystallographic 2-fold axis. The angles formed between the THF plane and the planes spanned by Cl1–Cl1′–O3–O3′ and O1–O2–O3–O3′ are 133.5 and 44°, respectively. The dihedral angle between the two THFs is 87° and larger than that, e.g., in $VCl_3(THF)_3$ (64°).[30] Somewhat surprisingly, the V–OH_2 distance in **8** (207.3 (10) pm), where H_2O is trans to the vanadyl oxygen, is comparable to the respective values in other V^{IV} complexes containing ligated H_2O (e.g. 208.9 (3) pm in $[\{VOCl_2(OH_2)\}_2(\mu\text{-}Cl)_2]^{2-}$[31] and 208.3 (4) pm in the corresponding fluoro complex[32]) with the doubly bonded oxygen cis to H_2O.

The dehydration of 1,4-butanediol described above is the reverse reaction of the ether splitting, which has been known, inter alia, for the system VCl_4/diethyl ether,[33] and which we have now observed for THF in inert solvents when treated with $VOCl_3$. The ^{51}V NMR resonances in the THF/$VOCl_3$ system have been described earlier[7a,34] and associated with complexes of composition $[VOCl_{3-n}(THF)_m]Cl_n$. In the light of our more recent investigations, these results have to be, in part, reinterpreted: The $\delta(^{51}V)$ signal that is observed in a freshly prepared sample of THF/$VOCl_3$/$CDCl_3$, −36 ppm, corresponds to a red complex of composition $VOCl_3(THF)_m$ (m = 1 and/or 2) in rapid exchange with $VOCl_3$. This is evidenced by the minor upfield shift of $\delta(^{51}V)$ with respect to $VOCl_3$ (0 ppm) and the ^{1}H NMR pattern (Figure 7), which is that of THF, slightly shifted and broadened by coordination. After the solution was allowed to stand for several days at room temperature or when the solution was refluxed for several hours, another single ^{51}V resonance arises at −287 ppm, which belongs to a compound of composition $VOCl_2\{OR\}$ (type A_1 in Scheme I), with R = $CH_2CH_2CH_2CH_2Cl$ (**9**; ^{1}H NMR δ 6.0, 3.8, and 2.2 ppm; cf. Figure 7). Hence, ether splitting here is conducted by simultaneous coordination of the splitting product and transfer of Cl from vanadyl chloride to C4:

$$VOCl_3 + THF \rightarrow \underset{\mathbf{9}}{VOCl_2O(CH_2)_3CH_2Cl}$$

Conclusion

As shown by ^{51}V NMR, vanadyl alkoxides $VO(OR)_3$ tend to associate in nonpolar media at concentrations > 0.01 mol/L. The tendency to associate is more pronounced if R is a sterically nondemanding alkyl. The extent of oligomerization shifts and the solid-state structures for R = Me[23] and CH_2CH_2Cl (this work) suggest that only for the very smallest R, viz. the methyl group, are well-defined dimers present, while oligomers consisting of two or more molecules, loosely connected through V–OR bonds and with a trigonal-bipyramidal arrangement for the monomeric unit, are the more general case. $VO(CH_2CH_2Cl)_3$ is one of the rare examples where the trigonal-bipyramidal geometry for V^V has been established, and it is the only *bona fide* example for an ester of orthovanadic acid. This compound may therefore be considered to model the pentavalent transition state for phosphorus in enzymatic phosphorylations and the regulatory effect of vanadate toward this type of reaction.[4a–e]

The mono- and dinuclear complexes formed with diols and diolates and containing the $VOCl_2\{OR\}$ and $VOCl\{OR\}_2$ units exhibit, in special cases (R = $CH_2CH_2CH_2CH_2OH$), interesting redox properties. The formation of $V^{IV}OCl_2(THF)_2(H_2O)$ from $V^VOCl_2O(CH_2)_3CH_2OH$ and 1,4-butanediol and the chlorination of THF by $VOCl_3$ to form $VOCl_2O(CH_2)_3CH_2Cl$ may be of relevance for a better understanding of the mechanistics of oxidation catalysts based on V^V[3] and of biocatalysts such as vanadate-dependent haloperoxidases.[35]

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Supplementary Material Available: Listings of atomic coordinates and anisotropic temperature factors (2 pages); listings of calculated and observed structure factors (36 pages). Ordering information is given on any current masthead page.

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