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Halide Abstraction from VCl_3 by $ZnCl_2$. Crystal Structure of $VCl_3 \cdot ZnCl_2 \cdot 4THF \cdot 2H_2O$

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Reaction of VCl_3 with $ZnCl_2$ in THF yields a material shown by elemental analysis, redox titration, infrared spectroscopy, and powder X-ray diffraction to be [*trans*-$VCl_2(THF)_4$][$ZnCl_3(THF)$], containing the tetrahedral anion $ZnCl_3(THF)^-$. The crystal structure of a derived material, $VCl_3 \cdot ZnCl_2 \cdot 4THF \cdot 2H_2O$, shows it to be composed of *trans*-$VCl_2(THF)_2(H_2O)_2^+$, $ZnCl_3(THF)^-$, and THF, all of which are linked together in chains by hydrogen bonding from the four aquo hydrogens of the cation to the three chloro ligands on zinc as well as to the lattice THF oxygen. All coordinated THF molecules are found to be planar at oxygen, an effect that is responsible for the Zn–O distance found here being 0.1 Å shorter than in $ZnCl_3(THF)^-$ observed elsewhere. The crystal form is triclinic, $P\bar{1}$, with (−162 °C) $a = 8.330$ (3) Å, $b = 20.222$ (9) Å, $c = 8.161$ (2) Å, $\alpha = 98.50$ (2)°, $\beta = 97.82$ (2)°, $\gamma = 99.85$ (2)°, and $Z = 2$.

Introduction

The frequently dramatic and sometimes beneficial influence of electropositive metals on the olefin polymerization activity of early-transition-metal compounds is widely recognized but poorly understood.[1] Electropositive metals may be incorporated by reduction of an early-transition-metal halide with an aluminum, magnesium, or zinc alkyl or by reduction with the elemental electropositive metal. Alternatively, it is possible to simply add a halide or alkoxide of Al(III), Mg(II), or Zn(II) to a reduced transition-metal halide.

We have reported on the nature of bimetallic compounds produced in THF when (1) VCl_3 is reduced by metallic Zn[2] and (2) $TiCl_3$ is reacted with $ZnCl_2$.[3] We have also noted[3] that such reactions sometimes produce materials with direct (i.e. ligand-bridged) connection between the different metals but other times yield ionic solids in which the metals segregate themselves into ions of opposite charge. We continue our exploration of this topic here with an examination of the nonredox reaction of VCl_3 with $ZnCl_2$.

Experimental Section

General Considerations. Tetrahydrofuran was purified by refluxing with potassium metal or Na/K/benzophenone under nitrogen. All operations were carried out under a nitrogen atmosphere, with use of either glovebox, Schlenk, or pressure bottle techniques. Anhydrous $ZnCl_2$ was obtained by the method of Pray,[4] and anhydrous VCl_3 was commercial material. Powder patterns were recorded with Cu Kα radiation on a Philips Norelco powder diffractometer equipped with a graphite monochromator.

Analysis. Vanadium(III) reduces Ag^+ and thus interferes with the determination of chloride. Consequently, Volhard method chloride determinations were carried out on solutions that had first been air oxidized for several days. Vanadium oxidation-state determination was by reduction of excess KIO_3, followed by assay for unreduced iodate by iodometry. Zinc and vanadium were estimated by plasma emission.

$VCl_3 \cdot ZnCl_2 \cdot 5THF$. $ZnCl_2$ (2.41 g, 17.6 mmol) and VCl_3 (2.78 g, 17.6 mmol) were refluxed in 75 mL of THF for 6 h. After about 1 h the initial slurry became an orange solution but it turned green-brown after 6 h. This solution is filtered hot and allowed to cool overnight, during which time a green solid precipitates. This solid is filtered and vacuum-dried, yielding 6.5 g (56%) of $VCl_3 \cdot ZnCl_2 \cdot 5THF$. The yield can be increased by concentration of the filtrate. Anal. Calcd for $C_{20}H_{40}Cl_5O_5VZn$: Cl, 27.10; V, 7.79; Zn, 9.99. Found: Cl, 27.03; V, 8.10; Zn, 10.28. Vanadium oxidation state: 2.97. IR (cm^{-1}, Nujol): ν_{COC} frequencies of THF at 830 (s, br), 880 (m), 997 (s), 1033 (m). Reflectance spectrum (nm): 475, 685.

Crystallographic Study. A suitable fragment of crystals grown by evaporation of a THF solution of $VCl_3 \cdot ZnCl_2 \cdot 5THF$ under a flow of argon was cleaved, under nitrogen, to obtain a nearly equidimensional fragment. The sample was then affixed to a glass fiber on a goniometer head and transferred to the goniostat, where it was cooled to −162 °C for characterization and data collection.

Table I. Crystal Data for $[VCl_2(THF)_2(H_2O)_2][ZnCl_3(THF)] \cdot THF$

empirical formula	$[VC_8H_{20}Cl_2O_4][ZnCl_3(THF)] \cdot THF$
color of cryst	green
cryst dimens, mm	0.12 × 0.12 × 0.14
space group	$P\bar{1}$
cell dimens (−162 °C, 30 reflcns)	
a, Å	8.330 (3)
b, Å	20.222 (9)
c, Å	8.161 (2)
α, deg	98.50 (2)
β, deg	97.82 (2)
γ, deg	99.85 (2)
molecules/cell	2
vol, Å^3	1321.05
calcd density, g/cm^3	1.554
wavelength, Å	0.710 69
mol wt	618.04
linear abs coeff, cm^{-1}	18.1
no. of unique intens	3455
no. with $F > 3.00\sigma(F)$	2874
$R(F)$	0.0320
$R_w(F)$	0.0336
goodness of fit for the last cycle	0.817
max Δ/σ for last cycle	0.05

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no systematic absences or symmetry, indicating the triclinic space group $P1$ or $P\bar{1}$. Statistical tests and the successful solution and refinement of the structure confirmed the $P\bar{1}$ centrosymmetric choice.

Diffraction data were collected (6° ≤ 2θ ≤ 45°, −162 °C) and processed according to our usual procedures.[5] Characteristics of the data collection appear in Table I. Considerable difficulty was encountered in solving the structure. As seen in the data, there is a pseudocentering that is explained in the final solution. Initial attempts to phase the data using direct methods (MULTAN 78) led to solutions with unrealistically short metal–metal separations (ca. 2.1 Å). In addition, the Patterson map was ambiguous, with one large

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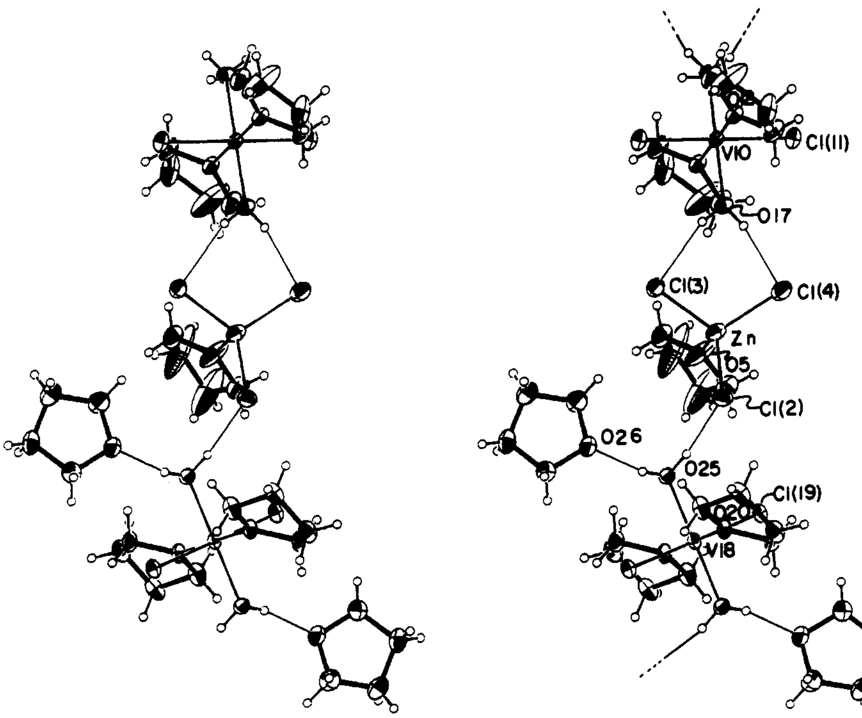

Figure 1. ORTEP stereo drawing of the hydrogen-bonded chain of $[VCl_2(THF)_2(H_2O)_2][ZnCl_3(THF)]\cdot THF$. The center of symmetry at V(10) continues the hydrogen bonding at the top with bonds to two chlorines (Cl(3)′ and Cl(4)′) of the next $ZnCl_3(THF)^-$. The center of symmetry of V(18) continues the hydrogen bonding at the bottom with a bond to Cl(2)′ of the next $ZnCl_3(THF)^-$.

Table II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $[VCl_2(THF)_2(H_2O)_2][ZnCl_3(THF)]\cdot THF$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Zn(1)	7976 (1)	2473.7 (2)	10073 (1)	23
Cl(2)	7923 (1)	3409 (1)	8945 (2)	28
Cl(3)	6711 (1)	1495 (1)	8361 (1)	27
Cl(4)	10473 (1)	2398 (1)	11397 (1)	29
O(5)	6548 (5)	2564 (2)	11882 (5)	48
C(6)	5195 (7)	2043 (3)	12066 (7)	33
C(7)	4908 (12)	2264 (5)	13749 (9)	97
C(8)	5419 (12)	2990 (5)	14099 (12)	99
C(9)	6773 (7)	3160 (3)	13171 (7)	31
V(10)	10000*	0*	10000*	15
Cl(11)	12270 (1)	510 (1)	12062 (1)	22
O(12)	8471 (3)	119 (1)	11685 (3)	19
C(13)	7059 (7)	−401 (3)	11886 (7)	29
C(14)	6543 (7)	−132 (3)	13485 (7)	39
C(15)	7546 (11)	535 (3)	14110 (9)	67
C(16)	8557 (7)	736 (3)	12903 (6)	31
O(17)	9810 (4)	928 (2)	9401 (4)	19
V(18)	5000*	5000*	0*	15
Cl(19)	7020 (1)	5069 (1)	2327 (1)	20
O(20)	3240 (3)	4880 (1)	1453 (3)	18
C(21)	1671 (5)	4376 (2)	1006 (6)	25
C(22)	920 (6)	4419 (3)	2585 (6)	28
C(23)	1570 (5)	5151 (3)	3439 (6)	25
C(24)	3329 (5)	5270 (3)	3140 (5)	25
O(25)	5200 (4)	6030 (1)	480 (4)	18
O(26)	7124 (4)	6937 (2)	2861 (4)	28
C(27)	7222 (7)	7610 (3)	2452 (7)	31
C(28)	8630 (7)	8054 (3)	3702 (7)	32
C(29)	8656 (6)	6901 (3)	3870 (7)	33
C(30)	9783 (6)	7582 (3)	4041 (7)	29

[a] Parameters marked by an asterisk are fixed by symmetry.
[b] Isotropic values are calculated by using the formula given by: Hamilton, W. C. *Acta Cryst.* 1959, *12*, 609.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[VCl_2(THF)_2(H_2O)_2][ZnCl_3(THF)]\cdot THF$

Zn–Cl(2)	2.2265 (15)	O(17)–H(17)	0.85 (6)
Zn–Cl(3)	2.2467 (16)	Cl(4)–H(17)	2.26 (8)
Zn–Cl(4)	2.2507 (16)	O(17)–H(18)	0.77 (5)
Zn–O(5)	2.025 (3)	Cl(3)–H(18)	2.32 (4)
V(10)–Cl(11)	2.3292 (14)	O(25)–H(27)	0.82 (6)
V(10)–O(12)	2.0135 (26)	O(26)–H(27)	1.82 (9)
V(10)–O(17)	2.034 (3)	O(25)–H(28)	0.89 (5)
V(18)–Cl(19)	2.3301 (13)	Cl(2)–H(28)	2.20 (4)
V(18)–O(20)	2.0125 (26)	mean C–O	1.456
V(18)–O(25)	2.035 (3)	mean C–C	1.477

Cl(2)–Zn–Cl(3)	114.87 (6)
Cl(2)–Zn–Cl(4)	114.85 (5)
Cl(2)–Zn–O(5)	104.14 (11)
Cl(3)–Zn–Cl(4)	111.90 (5)
Cl(3)–Zn–O(5)	103.83 (10)
Cl(4)–Zn–O(5)	105.82 (14)
Cl(11)–V(10)–O(12)	89.62 (9)
Cl(11)–V(10)–O(17)	89.97 (11)
O(12)–V(10)–O(17)	89.66 (11)
Cl(19)–V(18)–O(20)	90.08 (8)
Cl(19)–V(18)–O(25)	90.18 (10)
O(20)–V(18)–O(25)	89.22 (11)
Zn(1)–O(5)–C(6)	124.7 (3)
Zn(1)–O(5)–C(9)	123.90 (27)
C(6)–O(5)–C(9)	111.4 (4)
V(10)–O(12)–C(13)	125.82 (25)
V(10)–O(12)–C(16)	125.65 (25)
C(13)–O(12)–C(16)	108.5 (3)
V(18)–O(20)–C(21)	125.48 (24)
V(18)–O(20)–C(24)	125.30 (24)
C(21)–O(20)–C(24)	109.2 (3)

peak in a general position and numerous others due to other interactions. The structure was finally solved by dropping all zonal data and rephasing. Once the two metal atoms at centers of symmetry were located, all remaining atoms were easily located in difference Fouriers. All hydrogen atoms were located and refined isotropically. A final difference Fourier was featureless, the largest peak being 0.27 e/Å^3. No attempt was made to correct for absorption. The results of the structure determination appear in Tables II and III and Figure 1. Additional data has been deposited as Supplementary material.

Subsequent examination of this recrystallized material revealed electronic spectral transitions (by reflectance) at 445 and 675 nm.

Powder Diffraction. A comparison of the X-ray powder diagrams of authentic (i.e. anhydrous) $VCl_3\cdot ZnCl_2\cdot 5THF$ and $TiCl_3\cdot ZnCl_2\cdot 5THF$ (shown previously[3] by single-crystal X-ray diffraction to be [*trans*-$TiCl_2(THF)_4$][$ZnCl_3(THF)$]) shows them to be isomorphous. The diffraction data to $2\theta = 24°$ are shown in Table IV.

Table IV. X-ray Powder Pattern Data

$VCl_3 \cdot ZnCl_2 \cdot 5THF$		$TiCl_3 \cdot ZnCl_2 \cdot 5THF$	
d_{obsd}, Å	rel intens	d_{obsd}, Å	rel intens
10.7	13	10.9	6
9.30	7	9.40	7
8.34	6	8.34	6
7.43	70	7.49	100
7.02	7	7.02	11
6.27	50	6.32	79
5.40	100	5.50	76
5.18	9	5.24	16
5.09	38	5.15	33
4.50	7	4.52	17
4.37	53	4.43	39
4.27	13	4.30	41
4.17	92	4.23	85
4.04	9	4.07	14
3.75	67	3.80	69

Results

Synthesis. The reaction of reddish purple VCl_3 with equimolar $ZnCl_2$ in refluxing THF occurs via a color change to green and (upon cooling) deposition of a microcrystalline light green solid. Elemental analysis and oxidation-state determination are consistent with the formulation $VCl_3 \cdot ZnCl_2 \cdot 5THF$. The infrared spectrum shows two asymmetric and two symmetric ν(COC) stretching vibrations, indicative of THF in two distinct environments. We have reported[3] the preparation and structure of $TiCl_3 \cdot ZnCl_2 \cdot 5THF$, finding it to be composed to *trans*-$TiCl_2(THF)_4^+$ and $ZnCl_3(THF)^-$. An X-ray powder pattern of $VCl_3 \cdot ZnCl_2 \cdot 5THF$ shows it to be isomorphous with $TiCl_3 \cdot ZnCl_2 \cdot 5THF$; the *d* spacings out to at least 40° in 2θ are very similar, with only the diffracted intensities differing between the two compounds. We conclude that the vanadium compound reported here contains *trans*-$VCl_2(THF)_4^+$ and $ZnCl_3(THF)^-$, thus explaining the two THF types indicated by the infrared spectrum. The infrared spectra of $MCl_3 \cdot ZnCl_2 \cdot 5THF$ (M = Ti and V) are superimposable on one another.

Structural Study. The isomorphism of $TiCl_3 \cdot ZnCl_2 \cdot 5THF$ and the vanadium analogue was only established after the single-crystal X-ray study[3] of $TiCl_3 \cdot ZnCl_2 \cdot 5THF$ had been completed. Prior to that time, attempts were being made simultaneously to grow single crystals of both the Ti and V compounds. An attempt to grow crystals from a THF solution of $VCl_3 \cdot ZnCl_2 \cdot 5THF$ by solvent evaporation under a slow flow of cylinder argon yielded large green plates. Since these plates were *not* isomorphous with $TiCl_3 \cdot ZnCl_2 \cdot 5THF$, a decision was made to proceed with a single-crystal structural determination in order to establish the nature of this new solid.

The X-ray diffraction study establishes that the compound that was crystallized is comprised of equal amounts of *all-trans*-$VCl_2(THF)_2(H_2O)_2^+$, $ZnCl_3(THF)^-$, and uncoordinated THF units (Figure 1). $ZnCl_3(THF)^-$ lies in a general position, while *two* crystallographically *independent* $VCl_2(THF)_2(H_2O)_2^+$ units each lie on crystallographic centers of symmetry; this special position decreases the number of such cations of either type (V(10) and V(18)) such that the total numbers of vanadium and zinc centers are equal. There are two uncoordinated ("lattice") THF molecules for every two vanadiums, but these are both associated with only one of the two crystallographically independent $VCl_2(THF)_2(H_2O)_2^+$ ions. This "association" takes the form of a hydrogen bond to one of the two protons on each of the water molecules coordinated to V18; these serve to cap off or terminate hydrogen bonding in the direction perpendicular to a chain of hydrogen bonding portrayed in the vertical direction in Figure 1 involving *all* of the remaining O–H bonds in the repeat unit. These hydrogen bonds link the various $VCl_2(THF)_2(H_2O)_2^+$ cations by employing all three chlorines of the $ZnCl_3(THF)^-$ ions, which interleave the V(III) cations. Cl(2) hydrogen bonds to the remaining proton on water O(25), while Cl(3) and Cl(4) hydrogen bond to both protons of water O(17). In short, all hydroxyl protons are involved in hydrogen bonding, but none of the V–Cl ligands serve as donors in such bonds. The donors are three zinc-bound chlorides and the "lattice" THF oxygen, with all four O–(H)···Cl distances being in the range 3.066–3.091 Å; the O–(H)···O distance is 2.608 Å. The refined hydrogen atom positions in these three-center interactions are highly asymmetric; the close hydrogen association is uniformly with the water oxygen. The hydrogen bond angles O–H–acceptor are all either 161 or 167°.

The $ZnCl_3(THF)^-$ ion exhibits a systematic (threefold symmetric) deviation from tetrahedral symmetry (average values $\angle$Cl–Zn–Cl = 113.87°, $\angle$O–Zn–Cl = 104.60°) in response to the presence of the THF ligand. The THF oxygen (O(5)) is only 0.006 Å from the plane of its three attached atoms and thus coordinates in an effectively planar fashion.

The two independent V–Cl distances are identical within 1σ. The same holds for the two V–OH_2 distances and also the V–OC_4H_8 distances. All *cis*-(ligand)–V–(ligand) angles differ negligibly from 90°, yielding octahedral geometry about both metals in the *all-trans*-$VCl_2(THF)_2(H_2O)_2^+$ cations. The THF ligands in each cation (as judged by the C–O–C plane) are rotated by 44° from the corresponding V–Cl line, seemingly to minimize cis ligand–ligand repulsions. This steric argument is reinforced by the observation that the (smaller) water molecules are not staggered with respect to the cis ligands but in fact eclipse the V–Cl bonds. The coordinated water molecules are pyramidal at oxygen in spite of their involvement in hydrogen bonding. In contrast, the THF oxygens are essentially coplanar (±0.01 Å) with their attached atoms. As we have argued previously,[3] this is suggestive of some degree of four-electron donation by THF.

The three independent THF rings determined here have envelope (on V(10) and Zn) and twist (on V(18)) conformations.

The unexpected appearance of coordinated water in the sample crystallized for X-ray diffraction was supported by infrared spectroscopic data (Nujol mull) on these same crystals. While these crystals show four C–O–C stretching vibrations that duplicate those of $VCl_3 \cdot ZnCl_2 \cdot 5THF$, they also show a broad (full width at half height $\Delta\nu_{1/2}$ = 80 cm^{-1}) HOH bending absorption centered at 1625 cm^{-1} and an extremely broad ($\Delta\nu_{1/2}$ = 500 cm^{-1}) stretching vibration with a flat maximum from 3100 to 3400 cm^{-1}. The breadth and low energy of the stretching motion is particularly diagnostic of hydrogen bonding.[6,7] By way of contrast, authentic $VCl_3 \cdot ZnCl_2 \cdot 5THF$ shows no absorption around 1630 cm^{-1} and none above 3100 cm^{-1}. The presence of water vapor in the cylinder argon appears to us as the probable origin of the aquo ligands. We have observed that microcrystalline $VCl_3 \cdot ZnCl_2 \cdot 5THF$ is highly hydroscopic, absorbing water and turning to liquid after 1 h in the air.

Discussion

Zinc(II) chloride behaves toward VCl_3 in THF as a halide-abstracting reagent, forming [*trans*-$VCl_2(THF)_4^+$][$ZnCl_3(THF)^-$], rather than forming any halide-bridged mixed-metal adduct. Besides the X-ray isomorphism of this compound to $TiCl_3 \cdot ZnCl_2 \cdot 5THF$, these Ti and V analogues have identical infrared C–O–C stretching frequencies. These frequencies are markedly different from those of *mer*-$MCl_3(THF)_3$ (M = Ti and V),[2,3] and infrared spectra provide a

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useful rapid fingerprint for distinguishing these compounds from each other, and thus from simple physical mixtures of $MCl_3(THF)_3$ + $ZnCl_2(THF)_2$.

The hygroscopic character of $[VCl_2(THF)_4][ZnCl_3(THF)]$ is responsible for the unanticipated formation and crystallization of $[VCl_2(THF)_2(H_2O)_2][ZnCl_3(THF)]\cdot THF$. It is noteworthy that this limited incorporation of water amounts to replacement of two of the four THF ligands coordinated to vanadium with retention of the *trans*-$VCl_2O_4^+$ coordination environment.

The *trans*-VCl_2O_4 coordination environment was assigned by Horner and Tyree[8] to the compounds $VCl_3\cdot 6H_2O$, $VCl_3\cdot 4H_2O$, and $KVCl_4\cdot 6H_2O$, on the basis of the average ligand field evident in the $^3T_{1g}(F) \rightarrow {}^3T_{2g}$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ optical transitions. A similar conclusion, based on electrical conductance, magnetic susceptibility, and ligand field transition energies, was reached by Casey and Clark[9] for the series of alcohol complexes $VCl_3\cdot 4ROH$. The electronic spectra reported by these workers match well the spectra reported here for $VCl_3\cdot ZnCl_2\cdot 5THF$ and $VCl_3\cdot ZnCl_2\cdot 4THF\cdot 2H_2O$, which are themselves quite similar. A recent examination[10] of $Cs_3VCl_6\cdot 4H_2O$, including a diffraction study, shows this to contain *trans*-$VCl_2(H_2O)_4^+$.

Hydrogen bonding dominates the packing of the ionic units in solid $[VCl_2(THF)_2(H_2O)_2][ZnCl_3(THF)]\cdot THF$ and is responsible for the adoption of a space group distinct from that seen in the Ti and V compounds $MCl_3\cdot ZnCl_2\cdot 5THF$. The trans disposition of water molecules in the cation leads naturally to one-dimensional hydrogen-bonded chains, and the limitation that $ZnCl_3(THF)^-$ forms only three hydrogen bonds (i.e. three Cl^- sites) would leave one water hydrogen unused. However, the general principle that *all* acidic hydrogens be involved in hydrogen bonding[6,7] rigidly fixes the stoichiometry as that of a THF monosolvate. The observed O···acceptor distances (O–H···Cl from 3.066 to 3.091 Å and O–H···O = 2.608 Å) are each near the short end of typical[7] hydrogen bond distances. The near-linearity at hydrogen in these interactions is also typical. The possibility of symmetrical positioning of the hydrogen is only realized for "very short" O···H–O bonds, in the range of O–O separations of 2.4–2.5 Å. Such is not the case in $[VCl_2(THF)_2(H_2O)_2][ZnCl_3(THF)]\cdot THF$.

The $ZnCl_3(THF)^-$ ion found here closely duplicates Zn–Cl distances and interligand angles found in the absence of hydrogen bonding.[3] A major difference is found, however, in the Zn–O distance, being here 2.025 (3) Å, or 0.096 Å (11σ) shorter than that seen earlier[3] (2.121 (8) Å). This distinction appears to be related to the fact that the donor oxygen is planar here, whereas it is highly pyramidal in $[TiCl_2(THF)_4][ZnCl_3(THF)]$. Since numerous Zn(II) complexes exceed 18 valence electrons, it is permissible to attribute shortening of the Zn–O bond to O→Zn π donation.

The V–Cl distances in $[VCl_2(THF)_2(H_2O)_2][ZnCl_3(THF)]\cdot THF$ are identical with the corresponding distances in *mer*-$VCl_3(THF)_3$.[11] In contrast, the average $V-OC_4H_8$ distance reported here, 2.013 (3) Å, is 0.048 Å (8σ) shorter than the corresponding value in *mer*-$VCl_3(THF)_3$, 2.061 (8) Å. It is noteworthy that, in *all-trans*-$VCl_2(THF)_2(H_2O)_2^+$, the $V-OC_4H_8$ distance is 0.022 Å (7σ) *shorter* than the $V-OH_2$ distance, suggesting that THF is a better π donor than hydrogen-bonded water.

Two points warrant mention in regard to the structure of $[VCl_2(THF)_2(H_2O)_2][ZnCl_3(THF)]\cdot THF$. First, the water molecules preferentially bind to V(III), not Zn(II). Second, we have a repeat appearance of the $ZnCl_3(THF)^-$ ion, seen before in $[TiCl_2(,tHF)_4][ZnCl_3(THF)]$. In contrast, the $V_2(\mu\text{-}Cl)_3(THF)_6^+$ ion crystallizes from THF with the dimeric $Zn_2Cl_6^{2-}$ anion.[2,11] It is probable that the available cation precipitates with a zinc anion of comparable size (i.e. (monomer)$^+$(monomer)$^-$, (dimer)$^+$(dimer)$^-$). The consistent pattern emerging[3] is that THF promotes separation of cation and anion in the interaction of early-transition-metal chlorides with zinc chloride. Molecular adducts, $M(\mu\text{-}Cl)_2Zn^{II}Cl_m(THF)_n$, are not isolated.

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Supplementary Material Available: Listings of hydrogen positional parameters, anisotropic thermal parameters, C–C and C–O distances, and observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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