first homologue of (μ_4-Ge)[$Co_2(CO)_7$]$_2$. Gentle decarbonylation of $Ge_2Co_6(CO)_{20}$ gives the new [μ_4-$(CO)_4CoGe$]$_2Co_4(CO)_{11}$ cluster, a group 14 example in the octahedral $E_2M_4(CO)_n$ series.

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Registry No. $Co_2(CO)_8$, 15226-74-1; Me_3GeGeH_3, 20478-15-3; $Me_3GeCo(CO)_4$, 52637-40-8; (μ_4-Ge)[$Co_2(CO)_7$]$_2$, 77018-35-0; Me_3SiGeH_3, 18365-18-9; Ge_2H_6, 13818-89-8; $Ge_2Co_6(CO)_{20}$, 84664-74-4; $(GeH_3)_2SiMe_2$, 20576-05-0; $(CO)_4CoSiMe_2OCCo_3(CO)_9$, 72622-29-8; GeH_4, 7782-65-2; [μ_4-$GeCo(CO)_4$]$_2Co_4(CO)_{11}$, 94890-86-5; Co, 7440-48-4; Ge, 7440-56-4.

Supplementary Material Available: Listings of thermal parameters and of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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Two Compounds Containing the Tris(μ-chloro)hexakis(tetrahydrofuran)divanadium(II) Cation. Preparation, Structures, and Spectroscopic Characterization

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The reduction of $VCl_3(THF)_3$ with metallic zinc, as reported several years ago by Hall, Schmulbach, and Soby, affords a bright green compound that we have shown, by elemental analysis (including X-ray fluorescence measurements) and X-ray crystallography, to be [$V_2(THF)_6(\mu$-$Cl)_3$]$_2$[Zn_2Cl_6] (**1**). This compound can be converted to [$V_2(THF)_6(\mu$-$Cl)_3$]BPh_4 (**2**), also light green. X-ray crystallographic studies of both of these compounds have shown that the dinuclear, unipositive cation consists of two *fac*-$VCl_3(THF)_3$ octahedra with a common triangular Cl_3 face. The V–V distance (in **1**) is 2.993 (1) Å. The two crystalline compounds are characterized by the following crystallographic constants: For **1** at −105 °C, the triclinic unit cell (space group $P\bar{1}$) has the dimensions $a = 11.485$ (4) Å, $b = 15.312$ (2) Å, $c = 10.786$ (2) Å, $\alpha = 71.07$ (2)°, $\beta = 99.10$ (2)°, $\gamma = 104.41$ (2)°, $V = 1731$ (1) Å^3, and $Z = 2$. For **2** at 22 °C, the monoclinic unit cell (space group $P2_1/c$) has dimensions $a = 16.67$ (1) Å, $b = 16.77$ (1) Å, $c = 19.21$ (1) Å, $\beta = 110.93$ (2)°, $V = 5019$ (12) Å^3, and $Z = 4$. The dinuclear cation has an electronic spectrum that is solvent dependent (for **1**). In the presence of THF it exhibits remarkable, intense double spin-flip transitions of a type previously seen only in an unusual solid-state situation.

Introduction

The report by Hall, Schmulbach, and Soby[1] in 1981 that reduction of vanadium(III) chloride in THF by metallic zinc afforded a vanadium(II) chloride compound attracted interest in this laboratory several years ago. The product of this reduction, which was presumed to be $VCl_2{\cdot}2THF$, proved to be a convenient starting material for the synthesis of other vanadium(II) and vanadium(III) compounds. However, in the course of our work with it we had occasion to question its proposed formulation. We also obtained excellent crystals, serendipitously by slow solvolysis of phosphine adducts. The combined results of the X-ray crystallographic study and X-ray fluorescence analysis for vanadium and zinc led us to the unequivocal identification of the compound as [$V_2(THF)_6(\mu$-$Cl)_3$]$_2$(Zn_2Cl_6), and we presented a brief but definitive report of this result in 1983.[2]

We have since done a great deal of additional work with this compound, in some of which it has been used as a preparative starting material from which products containing either vanadium alone[3,4] or vanadium and zinc together[5,6] have been obtained. We have also extended our studies of the [$V_2(THF)_6(\mu$-$Cl)_3$]$^+$ ion itself,[7] and in this paper we shall describe the properties of this dinuclear cation in more detail.

Experimental Section

All operations were performed under an atmosphere of argon by using standard Schlenk techniques and a double-manifold vacuum line. Tetrahydrofuran, benzene, and hexane were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless-steel canulae and/or syringes. Sodium tetraphenylboron was deaerated under vacuum at room temperature.

Elemental analyses were performed by Galbraith Microanalytical Laboratories. Source-excited X-ray fluorescence analysis was done with a 100-mCi ^{241}Am excitation source. X-rays emitted from the sample were detected and analyzed by a KEVEX lithium-drifted silicon detector [Si(Li)]. Detector output pulses were digitized and evaluated with a Nuclear Data ND66 pulse height analyzer. We thank Professor Emil Schweikert of this department for the X-ray fluorescence analysis. The UV–visible spectra were measured on a Cary 17D spectrometer at room temperature. The IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer.

[$V_2(\mu$-$Cl)_3(THF)_6$]$_2$(Zn_2Cl_6) (1). This compound was prepared according to the published procedure.[1,2] The purity of the bulk, bright green [$V_2(\mu$-$Cl)_3(THF)_6$]$_2$(Zn_2Cl_6) was checked by elemental analyses, X-ray fluorescence measurements for V and Zn, and infrared spectroscopy.

Anal. Calcd for $C_{48}H_{96}Cl_{12}O_{12}V_4Zn_2$: C, 35.47; H, 5.95; Cl, 26.18. Found: C, 35.89; H, 5.92; Cl, 26.71.

X-ray fluorescence for a 2:1 atom ratio of V to Zn: calcd, 1.56; found, 1.49.

IR (KBr, cm^{-1}): 2960 (s), 2880 (s), 1450 (s), 1340 (m), 1290 (m), 1248 (m), 1178 (m), 1025 (vs), 913 (m), 870 (s), 680 (m).

Vis λ, nm (ϵ, given per mole of $V_2Cl_3(THF)_6{}^+$): (CH_2Cl_2) 695 (13), 450 (10.5), 410 (8), 400 (sh) (6), 345 (4.5); (CH_2Cl_2 + THF, 9:1) 625 (13), 430 (sh) (14), 405 (35), 395 (23), 630 (21).

Crystallographic quality crystals of [$V_2(\mu$-$Cl)_3(THF)_6$]$_2$(Zn_2Cl_6) were obtained by a two-step procedure. First, [$V_2(\mu$-$Cl)_3THF)_6$]$_2$(Zn_2Cl_6) was reacted with PPh_3 in benzene to give [$V_2(\mu$-$Cl)_3(THF)_5(PPh_3)$]$_2$(Zn_2Cl_6), which in turn was dissolved in THF and carefully layered with hexane. Under these conditions the PPh_3 ligand is slowly displaced by THF to give excellent quality crystals of [$V_2(\mu$-$Cl)_3(THF)_6$]$_2$(Zn_2Cl_6).

[$V_2(\mu$-$Cl)_3(THF)_6$]$B(C_6H_5)_4$ (2). To a slurry of [$V_2(\mu$-$Cl)_3$-$(THF)_6$]$_2$(Zn_2Cl_6) (1.20 g, 0.74 mmol) in 75 mL of THF, prepared in a 250-mL Schlenk tube equipped with a magnetic stirrer, was added $NaB(C_6H_5)_4$ (0.51 g, 1.49 mmol). The solution became immediately clear and bright green in color. Stirring of the reaction mixture was continued at room temperature for 12 h, after which a flocculent white precipitate was formed. The solution was filtered through Celite 545 (Fisher Scientific Co.), carefully covered with ~150 mL of hexane, and placed in a refrigerator at 0 °C for several days. Green crystals were obtained that were isolated by filtration, washed three times with hexane,

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(1) Hall, V. H.; Schmulbach, C. D.; Soby, W. N. *J. Organomet. Chem.* **1981**, *209*, 69.

(2) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377.

(3) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3316.

(4) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 4042.

(5) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 4046.

(6) Cotton, F. A.; Duraj, S. A.; Roth, W. J.; Schmulbach, C. D. *Inorg. Chem.* **1985**, *24*, 525.

(7) A number of compounds containing this cation were prepared by L. E. Manzer at the Central Research Laboratories of E. I. du Pont de Nemours Co. prior to the work in this laboratory. In collaboration with Dr. Manzer we hope to publish reports on these compounds, which contain various chloroalkylaluminate anions, in the near future.

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Table I. Summary of Crystallographic Data

formula	$ZnV_2Cl_6O_6$-$C_{24}H_{48}$	$V_2Cl_3O_6C_{48}BH_{68}$
fw	812.62	960.13
space gp	$P\bar{1}$	$P2_1/c$
syst abs		$0k0$ ($k \neq 2n$), $h0l$ ($l \neq 2n$)
a, Å	11.485 (4)	16.67 (1)
b, Å	15.312 (2)	16.77 (1)
c, Å	10.786 (2)	19.21 (1)
α, deg	71.07 (2)	90.0
β, deg	99.10 (2)	110.93 (2)
γ, deg	104.41 (2)	90.0
V, Å^3	1731 (1)	5019 (12)
Z	2	4
d_{calcd}, g/cm^3	1.56	1.27
cryst size, mm	0.3 × 0.3 × 0.15	0.35 × 0.25 × 0.10
μ(Mo Kα), cm^{-1}	17.18	5.63
data collcn instrum	CAD-4	
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	
orientation reflcns: no.; range (2θ)	25; 13.10–25.02	25; 6.6–20.8
temp, °C	−105	22
scan method	ω–2θ	
data collcn range (2θ), deg	$4 \leqslant 2\theta \leqslant 50$	$4 \leqslant 2\theta \leqslant 36$
no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$	8323; 6407	1807; 825
no. of parameters refined	389	120
R^a	0.045	0.098
$R_w{}^b$	0.067	0.086
quality-of-fit indicator^c	1.92	1.97
largest shift/esd, final cycle	0.42	0.03
largest peak, e/Å^3	0.89	0.5

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

and dried under vacuum (reproducible yields 1.15 g, 82%). The compound decomposes immediately to a brown oily material when exposed to air.

Anal. Calcd for $C_{48}H_{68}Cl_3BO_6V_2$: C, 60.05; H, 7.13; Cl, 11.07; B, 1.16. Found: C, 57.77; H, 7.25; Cl, 11.46; B, 1.40.

IR (KBr, cm^{-1}): 3060 (w), 3035 (s), 2963 (s), 2878 (m), 1570 (s), 1473 (s), 1450 (m), 1422 (m), 1255 (m), 1180 (w), 1128 (w), 1100 (w), 1068 (w), 1025 (vs), 915 (w), 882 (s), 800 (w), 732 (vs), 705 (vs), 670 (m), 610 (s).

Vis λ, nm (ϵ) (THF): 622 (13), 430 (sh) (19), 405 (34), 395 (26), 365 (22).

Crystals, suitable for X-ray analysis, can be obtained by the procedure described above or by careful layering of a THF solution of $[V_2(\mu\text{-}Cl)_3(THF)_6]^+BPh_4^-$ with hexane at room temperature.

X-ray Crystallography. General procedures that have already been fully described elsewhere were used to determine the crystal structures.[8] The cell parameters and basic information about data collection and structure refinement are summarized in Table I. Polarization and Lorentz corrections were applied to the intensity data; absorption and extinction corrections were not made.

We have worked with several different compounds containing the $[V_2Cl_3(THF)_6]^+$ cation, and in every case extensive disorder in the THF ligands had a detrimental effect on the quality of the intensity data. For **1**, the problem was alleviated by collecting data at low temperature and very good structural characterization was achieved. In the case of **2**, one of the effects of the disorder was weak diffraction by the crystals and few data above 30° in 2θ were observed. However, despite this severe limitation, the available data allowed unequivocal determination of the content of the unit cell as well as recognition of all important structural features of the ions present. The species of interest, viz. $[V_2Cl_3(THF)_6]^+$, was, within the experimental error, identical with the one accurately defined in **1**.

$[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$ (1). The structure was solved by direct methods with the use of the program MULTAN 81. All remaining non-hydrogen atoms were then located in a difference Fourier map. Two of the THF rings exhibited partial disorder involving two carbon atoms within each ligand. A fractional occupancy of $^1/_2$ was assigned to each of the disordered atoms. Anisotropic thermal parameters were assigned to all atoms in the final stages of refinement.

$[V_2Cl_3(THF)_6]B(C_6H_5)_4$ (2). The structure was solved by direct methods by using program MULTAN 81. Subsequent series of isotropic least-squares refinements and difference Fourier syntheses revealed the rest of the structure. Although for each THF ligand only one orientation was clearly defined, the existence of disorder was apparent on the basis of high thermal parameters of the carbon atoms and the presence of significant residual electron density around the THF rings. The isotropic refinement of 241 parameters with 1074 reflections with $F_o^2 \geq 2\sigma(F_o^2)$ gave R = 0.125 and R_w = 0.126. To complete the refinement, a rigid-body approximation was applied to the THF and phenyl groups and the program SHELX 76 was used for that purpose. The positional parameters of atoms in the THF rings were refined until interatomic distances reached the following set values:[9] 1.475 and 1.490 Å for O–C and C–C bonds, respectively, and 2.36 Å for four pairs of nonadjacent atoms. Each phenyl ring was represented by a regular hexagon with a C–C separation equal to 1.395 Å. Refinement of the rigid rings was carried out so that all atoms in a ring had the same thermal parameter and the carbon atoms bonded to the boron atom were pivot points for unrestrained movement of the rest of the rings. Anisotropic thermal parameters were assigned to the vanadium and chlorine atoms. The difference Fourier map obtained after refinement to convergence contained no peaks of chemical significance. The residual electron density was located primarily in the vicinity of the THF ligands and was clearly attributable to the disorder.

The tables of observed and calculated structure factors as well as anisotropic thermal parameters, B's, for both compounds are given in the supplementary material.

Results and Discussion

Preparation and Chemistry. The reduction of VCl_3 in THF with metallic zinc is a smooth and convenient reaction affording a light green, microcrystalline product. Initially[1] it was supposed that this substance was $VCl_2 \cdot 2THF$ because its color indicated the presence of vanadium and chemical analysis for C, H, Cl, and metal (not specific for vanadium) were in accord with this formula. These same analytical data are, of course, in accord with the formula $V_4Zn_2Cl_{12} \cdot 12THF$, within the usual limits of error. It is only a metal-specific analysis (e.g., by X-ray fluorescence analyses for V and Zn) that the composition can be established by chemical analysis. Unfortunately, the preparation of the compound in the practical manner described[1] never affords crystals suitable for structure determination, although the material so obtained is of good chemical quality and highly useful for synthetic work.[1,3–6]

We have found that large, well-formed crystals, perfectly suited for structural study, can be obtained from solutions of phosphine adducts of "$VCl_2 \cdot 2THF$". The critical feature here is that solvolysis of the phosphine complexes by THF generates the product slowly and thus allows the growth of sizable crystals. It was, of course, necessary to establish that these larger crystals used for the X-ray study were in fact the same compound as the microcrystalline material ordinarily prepared. This was done by elemental analysis, including X-ray fluorescence analysis for the metals, and comparisons of UV–visible and infrared spectra.

It has also been shown that from the compound $[V_2(THF)_6(\mu\text{-}Cl)_3]_2(Zn_2Cl_6)$ it is possible to obtain $[V_2(THF)_6(\mu\text{-}Cl)_3][B(C_6H_5)_4]$ and that this contains the same dinuclear cation. The solubility properties of the two compounds differ, however, and this leads to some interesting results in studies of their UV–visible spectra, as will be shown below.

Structural Results. For both compounds, $[V_2(THF)_6(\mu\text{-}Cl)_3]_2(Zn_2Cl_6)$ (**1**) and $[V_2(THF)_6(\mu\text{-}Cl)_3][B(C_6H_5)_4]$ (**2**), the positional and isotropic-equivalent thermal vibration parameters are listed in Tables II and III, respectively. Important interatomic distances and angles for both complexes are given in Tables IV and V, respectively. Complete listings of bond distances and angles are included in the supplementary material. ORTEP drawings of the $[V_2Cl_3(THF)_6]^+$ and $Zn_2Cl_6{}^{2-}$ ions are shown in Figure 1. The dinuclear cation in **2** has a labeling scheme similar to that in **1**.

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(8) See, for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(9) Averaged values of interatomic distances as determined for the THF ligands in $MCl_3(THF)_3$ (M = V, Cr) were the basis of this selection. A report on these compounds will be published soon: Cotton, F. A.; Duraj, S. A.; Powell, G.; Roth, W. J., to be submitted for publication.

Table II. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$ (**1**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Zn	0.35578 (4)	0.45589 (3)	0.49949 (4)	2.407 (9)
V(1)	0.77202 (5)	0.21913 (4)	0.20816 (5)	1.78 (1)
V(2)	0.70589 (5)	0.00784 (4)	0.29943 (5)	1.77 (1)
Cl(1)	0.63415 (7)	0.11906 (5)	0.37872 (8)	2.10 (2)
Cl(2)	0.67244 (8)	0.11292 (6)	0.07436 (8)	2.36 (2)
Cl(3)	0.91028 (7)	0.10947 (6)	0.30946 (9)	2.32 (2)
Cl(4)	0.51953 (9)	0.40953 (6)	0.4516 (1)	3.26 (2)
Cl(5)	0.2270 (1)	0.4873 (1)	0.3238 (1)	4.33 (3)
Cl(6)	0.2786 (1)	0.35811 (8)	0.6822 (1)	3.91 (3)
O(1)	0.8517 (2)	0.3079 (2)	0.3289 (2)	2.16 (5)
O(2)	0.9023 (2)	0.3042 (2)	0.0696 (2)	2.42 (5)
O(3)	0.6528 (2)	0.3133 (2)	0.1097 (2)	2.53 (5)
O(4)	0.5322 (2)	−0.0796 (2)	0.2837 (2)	2.28 (5)
O(5)	0.7805 (2)	−0.0864 (2)	0.2394 (2)	2.80 (5)
O(6)	0.7301 (2)	−0.0828 (2)	0.4940 (2)	2.31 (5)
C(11)	0.8041 (4)	0.3876 (3)	0.3303 (4)	3.14 (8)
C(12)	0.8951 (4)	0.4313 (3)	0.4257 (4)	3.25 (9)
C(13)	0.9284 (4)	0.3433 (3)	0.5293 (4)	3.08 (9)
C(14)	0.9292 (4)	0.2776 (3)	0.4497 (4)	2.89 (8)
C(21)	0.9207 (5)	0.2792 (4)	−0.0441 (4)	4.6 (1)
C(22)	1.0219 (5)	0.3581 (4)	−0.1086 (5)	5.1 (1)
C(23)	1.1022 (5)	0.3767 (5)	0.0084 (5)	5.3 (1)
C(24)	1.0149 (4)	0.3591 (4)	0.1103 (4)	4.1 (1)
C(31)	0.6607 (4)	0.3683 (4)	−0.0287 (4)	4.1 (1)
C(32A)	0.5425 (8)	0.3833 (7)	−0.0864 (9)	4.3 (2)
C(32B)	0.5573 (8)	0.4234 (7)	−0.059 (1)	4.4 (2)
C(33A)	0.4612 (7)	0.3242 (8)	0.0211 (9)	4.6 (2)
C(33B)	0.454 (1)	0.3539 (9)	0.030 (1)	7.7 (3)
C(34)	0.5297 (4)	0.2986 (5)	0.1437 (5)	5.8 (1)
C(41)	0.4986 (4)	−0.1669 (3)	0.2462 (4)	3.24 (9)
C(42)	0.3747 (4)	−0.2119 (3)	0.2989 (5)	3.8 (1)
C(43)	0.3169 (4)	−0.1273 (3)	0.2692 (4)	2.88 (8)
C(44)	0.4220 (3)	−0.0436 (3)	0.2674 (4)	3.04 (9)
C(51)	0.8849 (3)	−0.1222 (3)	0.3126 (4)	2.56 (7)
C(52)	0.9675 (4)	−0.1140 (4)	0.2109 (5)	5.1 (1)
C(53A)	0.8769 (7)	−0.1316 (5)	0.0964 (6)	2.2 (1)
C(53B)	0.887 (1)	−0.079 (1)	0.072 (1)	7.8 (5)
C(54A)	0.8003 (7)	−0.0655 (6)	0.0955 (7)	3.1 (2)
C(54B)	0.7572 (8)	−0.0972 (7)	0.1092 (8)	4.3 (2)
C(61)	0.6694 (4)	−0.1815 (3)	0.5417 (4)	2.75 (8)
C(62)	0.7405 (4)	−0.2182 (3)	0.6713 (4)	3.00 (9)
C(63)	0.7707 (4)	−0.1329 (3)	0.7248 (4)	3.12 (9)
C(64)	0.7975 (4)	−0.0504 (3)	0.6019 (3)	2.60 (8)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Taking into account the higher experimental error for structure **2**, it is evident from Tables IV and V that with both compounds virtually identical geometrical parameters for the $[V_2Cl_3(THF)_6]^+$ cation have been obtained. Since compound **1** was defined crystallographically with much better accuracy, a detailed discussion of the cation structure will be based only upon the results determined for compound **1**. Each of the vanadium(II) atoms has an octahedral *fac* geometry. Together they form a confacial bioctahedron with the common face composed of chloride ligands.

The exact nature of the interaction between the vanadium atoms, which are 2.993 (1) Å apart, in an electronic sense is a question we shall turn to later on. In a purely pragmatic structural sense, there appears to be a net repulsive force between them, in view of the observed angles in the central $V(\mu\text{-}Cl)_3V$ moiety.[10] In an ideal confacial bioctahedron the expected Cl–V–Cl and V–Cl–V angles would be 90 and 70.53° whereas the actual ones are 87.2 and 74.4°, indicative of a slight pushing apart of the vanadium atoms. The $[Cr_2Cl_9]^{3-}$ ion, in which there are also two d^3 cations shows evidence of a far greater repulsive force, with angles of 85.8 and 76.4° and a Cr···Cr distance of 3.12 Å. This is, perhaps, attributable to the greater charge on the Cr^{3+} ions compared to the V^{2+} ions.

Table III. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $[V_2Cl_3(THF)_6]B(C_6H_5)_4$ (**2**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
V(1)	0.2801 (6)	0.3273 (5)	0.6708 (4)	5.5 (4)
V(2)	0.1599 (7)	0.1980 (5)	0.6764 (4)	5.0 (4)
Cl(1)	0.320 (1)	0.1927 (7)	0.7299 (6)	6.8 (6)
Cl(2)	0.1745 (9)	0.3321 (7)	0.7336 (6)	5.0 (6)
Cl(3)	0.173 (1)	0.2600 (7)	0.5639 (6)	6.9 (6)
O(1)	0.383 (2)	0.321 (2)	0.616 (2)	9.9 (8)*
C(11)	0.352 (2)	0.352 (2)	0.539 (2)	9.9 (8)*
C(12)	0.394 (2)	0.302 (2)	0.498 (2)	9.9 (8)*
C(13)	0.410 (2)	0.224 (2)	0.538 (2)	9.9 (8)*
C(14)	0.438 (2)	0.253 (2)	0.617 (2)	9.9 (8)*
O(2)	0.233 (3)	0.441 (1)	0.617 (1)	9.1 (7)*
C(21)	0.279 (3)	0.517 (1)	0.636 (1)	9.1 (7)*
C(22)	0.225 (3)	0.576 (1)	0.581 (1)	9.1 (7)*
C(23)	0.136 (3)	0.544 (1)	0.560 (1)	9.1 (7)*
C(24)	0.140 (3)	0.461 (1)	0.588 (1)	9.1 (7)*
O(3)	0.376 (2)	0.383 (1)	0.764 (2)	9.5 (8)*
C(31)	0.460 (2)	0.407 (1)	0.763 (2)	9.5 (8)*
C(32)	0.501 (2)	0.456 (1)	0.832 (2)	9.5 (8)*
C(33)	0.462 (2)	0.425 (1)	0.885 (2)	9.5 (8)*
C(34)	0.387 (2)	0.374 (1)	0.844 (2)	9.5 (8)*
O(4)	0.137 (2)	0.141 (2)	0.769 (1)	8.9 (7)*
C(41)	0.189 (2)	0.076 (2)	0.814 (1)	8.9 (7)*
C(42)	0.143 (2)	0.052 (2)	0.865 (1)	8.9 (7)*
C(43)	0.097 (2)	0.125 (2)	0.874 (1)	8.9 (7)*
C(44)	0.099 (2)	0.184 (2)	0.817 (1)	8.9 (7)*
O(5)	0.022 (2)	0.213 (2)	0.628 (1)	8.5 (7)*
C(51)	−0.043 (2)	0.153 (2)	0.626 (1)	8.5 (7)*
C(52)	−0.122 (2)	0.176 (2)	0.563 (1)	8.5 (7)*
C(53)	−0.114 (2)	0.264 (2)	0.556 (1)	8.5 (7)*
C(54)	−0.024 (2)	0.288 (2)	0.602 (1)	8.5 (7)*
O(6)	0.152 (2)	0.075 (2)	0.630 (2)	9.2 (8)*
C(61)	0.101 (2)	0.065 (2)	0.550 (2)	9.2 (8)*
C(62)	0.164 (2)	0.047 (2)	0.514 (2)	9.2 (8)*
C(63)	0.238 (2)	0.009 (2)	0.574 (2)	9.2 (8)*
C(64)	0.227 (2)	0.022 (2)	0.646 (2)	9.2 (8)*
B	0.264 (4)	0.736 (3)	0.264 (2)	4 (2)*
C(71)	0.163 (1)	0.698 (2)	0.219 (2)	4.9 (6)*
C(72)	0.113 (1)	0.729 (2)	0.149 (2)	4.9 (6)*
C(73)	0.028 (1)	0.704 (2)	0.115 (2)	4.9 (6)*
C(74)	−0.006 (1)	0.647 (2)	0.150 (2)	4.9 (6)*
C(75)	0.044 (1)	0.616 (2)	0.219 (2)	4.9 (6)*
C(76)	0.129 (1)	0.642 (2)	0.253 (2)	4.9 (6)*
C(81)	0.265 (3)	0.816 (1)	0.312 (2)	5.2 (6)*
C(82)	0.329 (3)	0.836 (1)	0.380 (2)	5.2 (6)*
C(83)	0.326 (3)	0.909 (1)	0.413 (2)	5.2 (6)*
C(84)	0.259 (3)	0.962 (1)	0.380 (2)	5.2 (6)*
C(85)	0.194 (3)	0.942 (1)	0.313 (2)	5.2 (6)*
C(86)	0.197 (3)	0.869 (1)	0.279 (2)	5.2 (6)*
C(91)	0.323 (2)	0.655 (1)	0.322 (2)	4.5 (6)*
C(92)	0.359 (2)	0.596 (1)	0.292 (2)	4.5 (6)*
C(93)	0.399 (2)	0.530 (1)	0.335 (2)	4.5 (6)*
C(94)	0.402 (2)	0.523 (1)	0.408 (2)	4.5 (6)*
C(95)	0.366 (2)	0.583 (1)	0.439 (2)	4.5 (6)*
C(96)	0.327 (2)	0.649 (1)	0.396 (2)	4.5 (6)*
C(101)	0.319 (2)	0.753 (2)	0.205 (2)	5.5 (6)*
C(102)	0.298 (2)	0.714 (2)	0.137 (2)	5.5 (6)*
C(103)	0.343 (2)	0.730 (2)	0.090 (2)	5.5 (6)*
C(104)	0.410 (2)	0.785 (2)	0.111 (2)	5.5 (6)*
C(105)	0.432 (2)	0.824 (2)	0.180 (2)	5.5 (6)*
C(106)	0.386 (2)	0.808 (2)	0.226 (2)	5.5 (6)*

[a] Starred values indicate atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

The mean V–Cl and V–O bond lengths are 2.478 [3] and 2.147 [7] Å, respectively. The former is considerably longer than the bond in another V(II) dimer containing chloride bridges, namely $[VCl(dppm)BH_4]_2$ with a V–Cl distance of 2.424 [2] Å.[4] The V–O bond may be compared with the one in *mer*-$VCl_3(THF)_3$.[2,9] For the oxygen trans to chlorine it is equal 2.102 (3) Å, and the shortening may be attributed to a stronger attraction of the oxygen atom with partial negative charge by the more positive V^{3+} center.

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(10) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

Table IV. Important Interatomic Distances (Å) for $[V_2Cl_3(THF)_6]_2(Zn_2Cl)_6$ (**1**) and $[V_2Cl_3(THF)_6]B(C_6H_5)_4$ (**2**)[a]

	1	2
V(1)-V(2)	2.993 (1)	2.981 (14)
-Cl(1)	2.475 (1)	2.509 (14)
-Cl(2)	2.472 (1)	2.47 (2)
-Cl(3)	2.474 (1)	2.464 (13)
-O(1)	2.129 (2)	2.31 (4)
-O(2)	2.155 (2)	2.17 (3)
-O(3)	2.148 (2)	2.14 (3)
V(2)-Cl(1)	2.485 (1)	2.50 (2)
-Cl(2)	2.472 (1)	2.476 (14)
-Cl(3)	2.481 (1)	2.47 (2)
-O(4)	2.124 (2)	2.16 (3)
-O(5)	2.152 (2)	2.16 (3)
-O(6)	2.127 (2)	2.23 (3)
Zn-Zn′	3.251 (1)	
-Cl(4)	2.349 (1)	
-Cl(4)′	2.361 (1)	
-Cl(5)	2.211 (1)	
-Cl(6)	2.211 (1)	

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The $[Zn_2Cl_6]^{2-}$ ion can be regarded as consisting of two $ZnCl_4$ tetrahedra sharing an edge. It shows evidence of marked cation–cation repulsion, as expected. The Zn···Zn distance is 3.251 (1) Å, and the Cl_{br}–Zn–Cl_{br} angle is only 92.70 (4)°, and the Cl_t–Zn–Cl_t angle is 116.31 (4)°, while the four Cl_{br}–Zn–Cl_t angles are in the range 108.27 (5)–114.60 (5)°. The Zn–Cl_{br} bond lengths are 2.349 (1) and 2.361 (1) Å while the Zn–Cl_t bond lengths are considerably shorter, both being 2.211 (1) Å.

Electronic Absorption Spectrum of the Divanadium Cation. As already mentioned, the nature of the electronic interaction between the two vanadium(II) ions is a question of particular interest. We hope to deal with it in detail in a future publication, but several observations will be presented here to show that some novel and significant factors come into play.

Figure 2 shows several spectra that we shall discuss. The set of spectra labeled a are all taken on solutions of compound **1** in solvents of different composition, while spectrum b is that of compound **2** measured in pure THF. It can be seen that the spectrum of **1** in pure CH_2Cl_2 is quite different from b, but that upon addition of a few drops of THF there is a change leading to a closer resemblence to the spectrum b. When another few drops of THF are added a spectrum nearly identical with b is obtained. Because the addition of a few drops of THF to the approximately 3.5-mL volume of solution used to record the spectra in group a causes a slight dilution, precise isosbestic points cannot be expected, but it is evident that we are dealing with an equilibrium between two chromophores, one of which is essentially the same as that in the pure THF solution of **2**. We believe that this chromophore is the $[V_2(THF)_6(\mu\text{-}Cl)_3]^+$ ion itself. It is to be noted that **1** will not dissolve in pure THF and **2** will not dissolve in CH_2Cl_2 so that the results presented in Figure 2 provide the only practical comparison of the spectra of the two compounds. It has been found that crystalline **1** and **2** both have spectra very similar to spectrum b; these solid-state studies are still incomplete and will not be discussed further at this time.

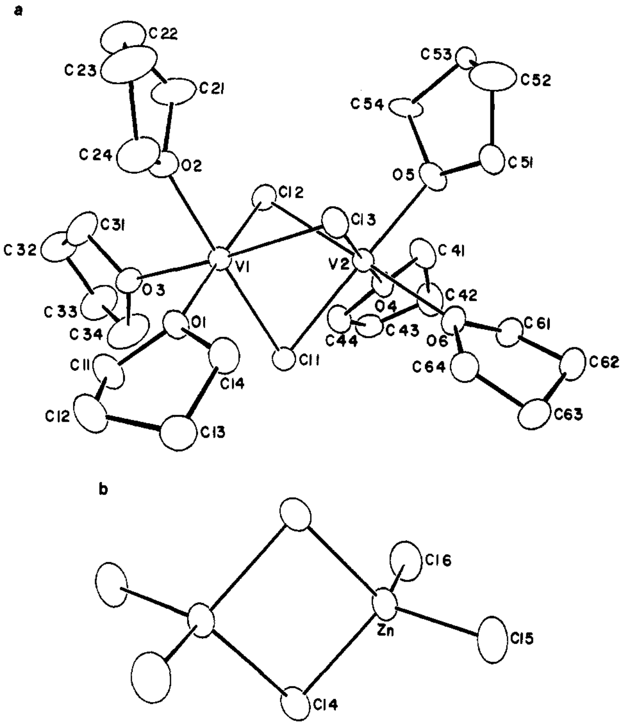

Figure 1. ORTEP drawing of the (a) $[V_2(\mu\text{-}Cl)_3(THF)_6]^+$ cation, and (b) $[Zn_2Cl_6]^{2-}$ anion.

We cannot say with certainty why the spectra of **1** show the solvent sensitivity that they do. Tentatively, we suggest that in pure CH_2Cl_2, where the solvating power is poor, strong (but reversible) cation–anion association occurs. A significant change in the structure of the cation, a change which, for reasons discussed below, entails a considerable reduction in coupling between the V^{2+} ions, is caused by this ion association. Upon addition of THF the character of the solvent becomes such that essentially unperturbed $[V_2(THF)_6(\mu\text{-}Cl)_3]^+$ ions become predominant and their characteristic spectrum is seen.

The spectrum of this dinuclear cation, however, is of unusual interest. It is by no means the spectrum we might expect if the

Table V. Important Bond Angles (deg) for the $[V_2Cl_3(THF)_6]^+$ Cation in **1** and **2**[a]

	1	2		1	2
Cl(1)-V(1)-Cl(2)	87.29 (3)	86.0 (6)	Cl(1)-V(2)-Cl(2)	87.07 (2)	86.0 (5)
-Cl(3)	87.39 (2)	87.8 (5)	-Cl(3)	87.02 (3)	87.7 (6)
-O(1)	90.31 (5)	93 (1)	-O(4)	94.67 (5)	97.0 (9)
-O(2)	176.04 (6)	174 (1)	-O(5)	175.73 (6)	175 (1)
-O(3)	94.62 (6)	90.8 (8)	-O(6)	92.07 (6)	92 (1)
Cl(2)-V(1)-Cl(3)	87.45 (3)	89.4 (6)	Cl(2)-V(2)-Cl(3)	87.31 (3)	88.9 (5)
-O(1)	177.55 (6)	178.0 (8)	-O(4)	91.27 (6)	93.1 (9)
-O(2)	94.81 (5)	90 (1)	-O(5)	95.07 (6)	90 (1)
-O(3)	90.11 (6)	91 (1)	-O(6)	178.56 (6)	177.2 (9)
Cl(3)-V(1)-O(1)	92.97 (5)	92.0 (8)	Cl(3)-V(2)-O(4)	177.74 (6)	175.0 (9)
-O(2)	89.35 (6)	88.4 (8)	-O(5)	89.40 (6)	89.4 (9)
-O(3)	176.76 (6)	178.4 (9)	-O(6)	93.80 (6)	93 (1)
O(1)-V(1)-O(2)	87.62 (7)	92 (2)	O(4)-V(2)-O(5)	88.97 (8)	86 (1)
-O(3)	89.55 (7)	87 (1)	-O(6)	87.65 (7)	85 (1)
O(2)-V(1)-O(3)	88.73 (8)	93 (1)	O(5)-V(2)-O(6)	85.86 (8)	92 (1)
			V(1)-Cl(1)-V(2)	74.24 (2)	73.1 (5)
			V(1)-Cl(2)-V(2)	74.53 (2)	74.2 (5)
			V(1)-Cl(3)-V(2)	74.32 (2)	74.3 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

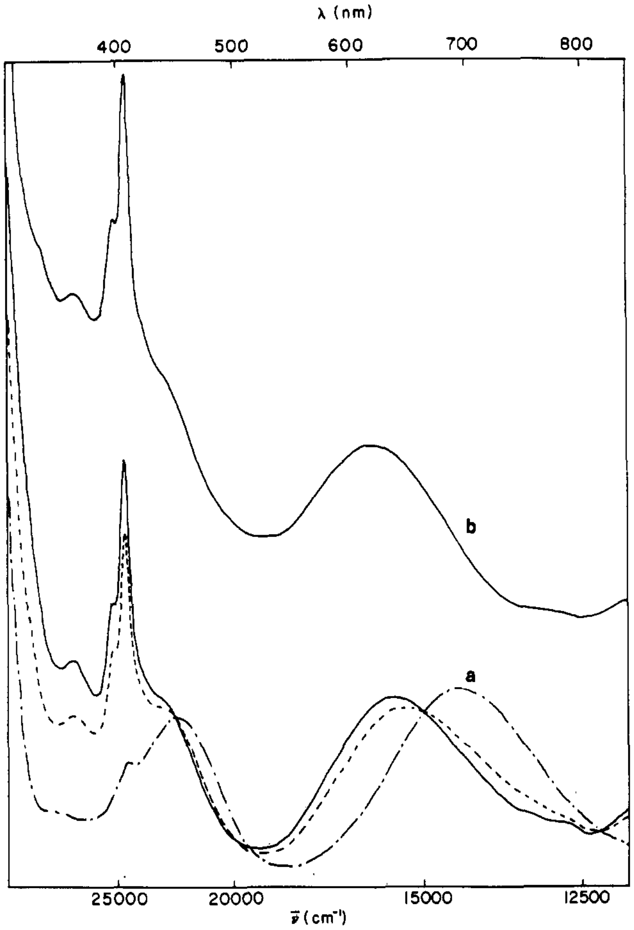

Figure 2. Visible spectra of **1** and **2** in the region 300–840 nm: (a) 0.02 M $[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$ in neat CH_2Cl_2 (–·–), after adding 2 drops of THF (---), and after adding 5 drops of THF (—); (b) 0.018 M $[V_2Cl_3(THF)_6]B(C_6H_5)_4$ in THF.

V^{2+} ions are essentially noninteracting. For a *fac*-$[VCl_3(THF)_3]^-$ ion we might invoke the average crystal field approach and combine available data for the $[VCl_6]^{4-}$ and $[V(H_2O)_6]^{2+}$ ions.[11] The spin-allowed, ligand field transitions should then appear, with band widths of ca. 2500 cm^{-1}, at about 10000 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{2g}$), about 15000 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{1g}$ (F)), and about 23000 cm^{-1} ($^4A_{2g} \rightarrow {}^4T_{1g}(P)$), where we use state designations based on true octahedral symmetry for the sake of simplicity. One might also expect very weak, sharp spin-forbidden transitions ($^4A_{2g} \rightarrow {}^2T_{1g}$, ^2E_g) at 12000–13000 cm^{-1}. While there are bands of appropriate widths approximately in the expected positions (the onset of the ca. 10000-cm^{-1} band can just be seen in Figure 2), there is a totally unpredicted feature that dominates the high-energy portion of the spectrum, nearly (but not entirely) obscuring the predicted $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transition. This is a strong sharp doublet at ca. 25000 cm^{-1}.

The sharpness of this doublet identifies it as a type of transition in which essentially no shift of electron density from bonding to antibonding orbitals occurs, so that no vibrational progression (which is the cause of the normal line shapes for crystal field transitions) occurs. Transitions of this type are generally spin-flip transitions, i.e., transitions in which only the spin quantum number changes but no orbital quantum number changes. However, such spin-flip transitions are spin forbidden and are usually very weak. The recognized spin-flip transitions for an isolated, octahedrally coordinated V^{2+} ion are the essentially degenerate $^4A_{2g} \rightarrow {}^2T_{1g}$, ^2E_g transitions expected at ca. 13000 cm^{-1}; there are, indeed, some extremely weak, narrow maxima to be seen in this region in Figure 2.

To account for the *strong*, sharp bands at ca. 25000 cm^{-1}, we propose that they be assigned to *double spin-flip* transitions of the coupled pair of V^{2+} ions. Crudely put, if there is an antiferromagnetic coupling of the two ions, it is possible to have a transition in which the spin-flip transitions at the two vanadium centers take place in concert, thus requiring approximately twice the energy, but with no change in the combined spin quantum number. Since $\Delta S = 0$, the transition is no more forbidden than a regular crystal field transition, but of course it still gives a narrow band because the electrons remain in the same orbitals.

It is remarkable that just as this paper was in preparation, a study of the spectra of V^{2+} ions doped into $CsMgCl_3$ appeared[12] in which analogous double spin-flip transitions were observed. At an appropriate level of doping (1–10%), a substantial number of adjacent Mg^{2+} sites are occupied by V^{2+} ions, thus creating what are in effect $Cl_3VCl_3VCl_3$ confacial bioctahedra. The advantage of studying these systems is that alignment of the anionic chains facilitates polarization measurements, but otherwise we believe our $[V_2(THF)_6(\mu\text{-}Cl)_3]^+$ compounds are more convenient subjects for study. For one thing we can be certain of the exact dimensions of the divanadium chromophore, and for another magnetic studies are feasible, which is not the case (or at least not very simply) with the $CsMg(V)Cl_3$ system. We shall report the results of such a study later.

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Registry No. **1**, 89172-48-5; **2**, 94820-20-9.

Supplementary Material Available: Listings of observed and calculated structure factors, bond distances and angles in addition to those given in the journal, and anisotropic thermal vibration parameters (46 pages). Ordering information is given on any current masthead page.

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[11] Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968; pp 273–274.

[12] Riesen, H.; Güdel, H. U. *Inorg. Chem.* **1984**, *23*, 1880.