

48 h at room temperature, about 95% of the nicotinate was still bound to chromium(III) (based on curve-fitting analysis). Assuming formation of a trans aqua nicotinate complex, 90% of the *trans*-[Cr(1,3-pn)₂(nic-O)₂]⁺ was still present. In addition, the visible spectrum obtained after 48 h showed ca. 5% decrease in absorption at 373 and 512 nm and ca. 3% increase at 423 nm (λ_{\min}). Since a trans aqua nicotinate complex is not expected to have a markedly different visible spectrum, it is difficult to estimate the amount of decomposition by visible spectroscopy. However, it is apparent from the NMR and visible spectral data that approximately 90% of the original complex was still present.

The stability of this complex appears to be due to the chelation of 1,3-pn to chromium(III). Unlike bis(ethylene-diamine) complexes of chromium(III), (1,3-pn)₂ complexes prefer a trans arrangement and do not show any evidence for partial dissociation of the chelate rings.⁹ Since substitution

of octahedral chromium(III) complexes proceeds by an associative mechanism,¹⁰ the bulkiness of the 1,3-pn chelate rings probably inhibits substitution. If there is a biologically active form of the chromium(III)-nicotinic acid complex, it may be stabilized by the ligand complement. For example, chromium(III)-bound nicotinic acid may be stabilized within a peptide or protein matrix.

Acknowledgment. We thank Donald Appel for his assistance in using the Nicolet NT-200. The Nicolet 200-MHz spectrometer was acquired with the aid of the Boeing Co. Partial support of this study by the USDA (Grant No. 82-CRCR-1-1005) is gratefully acknowledged.

Registry No. *trans*-[Cr(1,3-pn)₂(nic-O)₂]Cl, 91084-62-7; *trans*-[Cr(1,3-pn)₂(nic-O)₂]⁺ (deuterated), 91110-51-9; *trans*-[Cr(mal)₂(py-2-d)₂]⁻, 91084-66-1; deuterium, 7782-39-0.

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Notes

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Identification of the Zinc Reduction Product of VCl₃·3THF as [V₂Cl₃(THF)₆]₂[Zn₂Cl₆]

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Anhydrous vanadium trichloride is reduced by zinc in tetrahydrofuran (THF) to a material claimed first to be a mixture of VCl₂(THF)₂ and ZnCl₂·xTHF¹ and then later (exclusively on the basis of elemental analysis for Cl, C, H, and V) to be VCl₂(THF)₂.² This material is of substantial synthetic utility, leading to Cp₂V,¹ to V₂(fulvalene)₂,³ to a polynuclear vanadium carboxylate,⁴ and to Cp₂V₂C₈H₈.⁵ Our work⁶ with low-valent vanadium complexes led us to question the accuracy of this² characterization, and yet microscopic visual inspection of the crystalline material and visual observation of its reaction with O₂ (all crystals oxidize, suggesting the absence of ZnCl₂·xTHF crystals) suggested that it was homogeneous. We report here on the true identity of this material.

The chemistry of V(II), especially of V(II) dimers, is relevant to the efficient reduction of N₂ in alkaline protic media.⁷ Vanadium(II), both in aqueous solution⁸ and in THF,⁹ is a useful reagent for reduction of a variety of organic compounds.

Experimental Section

General Procedures and Materials. All experiments were carried out under nitrogen, by using Schlenk and drybox techniques and dried solvents. Temperature-dependent magnetic susceptibility measurements were performed on a Faraday system (Oxford Instruments) equipped with a Mettler ME 21 electronic vacuum microbalance. Vanadium was analyzed coulometrically¹⁰ as metavanadate after digestion with perchloric acid at 180 °C.¹¹ Zinc was analyzed by

Table I. Magnetic Susceptibilities of [V₂Cl₆(THF)₆]₂[Zn₂Cl₆] at Various Temperatures^a

T, K	10 ⁻⁶ χ _{mol} , cgsu	T, K	10 ⁻⁶ χ _{mol} , cgsu
32.3	469	106.4	2659
38.2	633	120.3	2944
44.8	831	140.2	3267
52.3	1073	160.2	3527
61.0	1372	180.6	3741
70.1	1668	200.1	3914
80.1	2000	225.0	4107
92.1	2337	250.1	4272

^a Susceptibilities are corrected for diamagnetism (χ_{mol,dia} = 520 × 10⁻⁶ cgsu) and a paramagnetic impurity (2% based on V²⁺).

using atomic absorption spectrophotometry after digestion with concentrated H₂SO₄/HNO₃.¹¹

Synthesis of [V₂(μ-Cl)₃(THF)₆]₂[Zn₂Cl₆]. A suspension of 1.70 g (26 mmol) of zinc powder and 4.16 g of VCl₃·3THF (11.1 mmol) in 35 mL of THF was stirred for 18 h at 25 °C. After the supernatant was decanted, the green product was dissolved in 30 mL of CH₂Cl₂. The solution was filtered and the solvent partly removed under vacuum. The product was precipitated with pentane. The resulting green powder was filtered, washed with pentane, and dried under vacuum; yield 4.10 g (2.52 mmol, 91%). Anal. Calcd for C₄₈H₉₆Cl₁₂O₂V₄Zn₂: C, 35.47; H, 5.95; Cl, 26.18; V, 12.54; Zn, 8.04. Found: C, 35.79; H, 6.08; Cl, 26.57; V, 12.60; Zn, 8.03. IR (Nujol, cm⁻¹): THF frequencies at 1343 (m), 1294

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Table II. Crystal Data for $[V_2Cl_3(THF)_6]_2Zn_2Cl_6$

empirical formula	$Zn_2V_4Cl_{12}O_{12}C_{48}H_{96}$
color (-160 °C)	bright blue
cryst dimens, mm	0.28 × 0.28 × 0.28
space group	$P\bar{1}$
cell dimens (-160 °C; 41 reflns)	
<i>a</i> , Å	11.444 (2)
<i>b</i> , Å	15.241 (4)
<i>c</i> , Å	10.771 (3)
α , deg	109.09 (1)
β , deg	98.61 (1)
γ , deg	75.66 (1)
molecules/cell	1
<i>V</i> , Å ³	1715.24
<i>d</i> _{calcd} , g/cm ³	1.57
λ , Å	0.710 69
mol wt	1625.24
linear abs coeff, cm ⁻¹	17.3
total no. of reflns colled ($6^\circ \leq 2\theta \leq 45^\circ$)	5195
no. of unique intns	4503
no. with <i>F</i> > 0.0	4361
no. with <i>F</i> > $\sigma(F)$	4290
no. with <i>F</i> > 2.33 $\sigma(F)$	4143
final residuals	
<i>R</i> (<i>F</i>)	0.0270
<i>R</i> _w (<i>F</i>)	0.0325
goodness of fit for the last cycle	1.046
max Δ/σ for last cycle	0.05

Table III. Fractional Coordinates and Isotropic Thermal Parameters^a for Non-Hydrogen Atoms in $[V_2Cl_3(THF)_6]_2Zn_2Cl_6$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å ²
V(1)	7722.0 (4)	2787.3 (4)	2078.0 (5)	12
V(2)	7078.7 (4)	4898.6 (4)	2978.0 (5)	12
Cl(3)	6345 (1)	3800 (1)	3806 (1)	15
Cl(4)	9126 (1)	3875 (1)	3061 (1)	16
Cl(5)	6720 (1)	3840 (1)	732 (1)	16
O(6)	9027 (2)	1922 (2)	672 (2)	17
C(7)	9209 (3)	2160 (3)	-472 (4)	28
C(8)	10244 (4)	1383 (3)	-1106 (4)	28
C(9)	11042 (4)	1247 (3)	86 (4)	33
C(10)	10163 (3)	1368 (3)	1084 (4)	23
O(11)	6540 (2)	1827 (2)	1099 (2)	16
C(12)	6589 (4)	1312 (3)	-300 (4)	26
C(13)	5488 (5)	933 (5)	-715 (5)	71
C(14)	4576 (4)	1645 (5)	218 (5)	58
C(15)	5320 (4)	1948 (3)	1447 (4)	32
O(16)	8527 (2)	1903 (1)	3290 (2)	14
C(17)	8060 (3)	1116 (3)	3327 (4)	23
C(18)	8945 (3)	691 (3)	4266 (3)	20
C(19)	9261 (3)	1562 (3)	5294 (3)	22
C(20)	9289 (3)	2204 (2)	4501 (3)	20
O(21)	7856 (2)	5816 (2)	2349 (2)	19
C(22)	8877 (3)	6214 (2)	3117 (3)	18
C(23)	9697 (3)	6161 (3)	2106 (4)	29
C(24)	8839 (4)	6243 (3)	922 (4)	31
C(25)	7956 (4)	5686 (3)	960 (4)	35
O(26)	5336 (2)	5788 (1)	2839 (2)	16
C(27)	5014 (3)	6646 (3)	2436 (4)	22
C(28)	3782 (3)	7112 (3)	2955 (4)	25
C(29)	3183 (3)	6274 (2)	2687 (3)	19
C(30)	4229 (3)	5433 (3)	2662 (4)	20
O(31)	7313 (2)	5821 (1)	4928 (2)	15
C(32)	6707 (3)	6809 (2)	5418 (3)	18
C(33)	7409 (3)	7175 (2)	6707 (3)	21
C(34)	7705 (3)	6333 (3)	7235 (3)	21
C(35)	7984 (3)	5500 (2)	6019 (3)	18
Zn(36)	3552.9 (3)	452.1 (3)	5007.7 (4)	16
Cl(37)	2787 (1)	1448 (1)	6856 (1)	26
Cl(38)	5205 (1)	901 (1)	4504 (1)	22
Cl(39)	2259 (1)	141 (1)	3255 (1)	30

^a Isotropic values for those atoms refined anisotropically are calculated with the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, 12, 609.

(m), 1256 (w), 1180 (m), 1022 (m, $\nu_{asym}(COC)$), 912 (s), 870 (vs, $\nu_{sym}(COC)$), 720 (m), 676 (m). UV-Vis (CH_2Cl_2 :THF = 2:1) λ , 10³

Table IV. Bond Distances (Å) for $[V_2Cl_3(THF)_6]_2Zn_2Cl_6$

Zn-Zn'	3.257 (1)	V(2)-Cl(3)	2.490 (1)
Zn-Cl(37)	2.218 (1)	V(2)-Cl(4)	2.480 (1)
Zn-Cl(38)	2.351 (1)	V(2)-Cl(5)	2.471 (1)
Zn-Cl(38')	2.363 (1)	V(1)-O(6)	2.158 (2)
Zn-Cl(39)	2.215 (1)	V(1)-O(11)	2.152 (2)
V(1)-V(2)	2.973 (1)	V(1)-O(16)	2.132 (2)
V(1)-Cl(3)	2.475 (1)	V(2)-O(21)	2.150 (2)
V(1)-Cl(4)	2.473 (1)	V(2)-O(26)	2.131 (2)
V(1)-Cl(5)	2.470 (1)	V(2)-O(31)	2.132 (2)

Table V. Bond Angles (deg) for $[V_2Cl_3(THF)_6]_2Zn_2Cl_6$

Cl(37)-Zn-Cl(38)	111.92 (4)	O(11)-V(1)-O(16)	89.5 (1)
Cl(37)-Zn-Cl(39)	116.51 (3)	Cl(3)-V(2)-Cl(4)	87.4 (0)
Cl(39)-Zn-Cl(38')	114.90 (4)	Cl(3)-V(2)-Cl(5)	87.3 (0)
Cl(37)-Zn-Cl(38')	108.00 (3)	Cl(3)-V(2)-O(21)	175.2 (1)
Cl(38)-Zn-Cl(38')	92.61 (3)	Cl(3)-V(2)-O(26)	94.5 (1)
Cl(38)-Zn-Cl(39)	110.46 (4)	Cl(3)-V(2)-O(31)	91.5 (1)
Cl(3)-V(1)-Cl(4)	87.9 (0)	Cl(4)-V(2)-Cl(5)	87.9 (0)
Cl(3)-V(1)-Cl(5)	87.7 (0)	Cl(4)-V(2)-O(21)	88.4 (1)
Cl(3)-V(1)-O(6)	176.0 (1)	Cl(4)-V(2)-O(26)	177.7 (1)
Cl(3)-V(1)-O(11)	95.2 (1)	Cl(4)-V(2)-O(31)	94.1 (1)
Cl(3)-V(1)-O(16)	90.1 (1)	Cl(5)-V(2)-O(21)	94.9 (1)
Cl(4)-V(1)-Cl(5)	88.0 (0)	Cl(5)-V(2)-O(26)	90.9 (1)
Cl(4)-V(1)-O(6)	88.9 (1)	Cl(5)-V(2)-O(31)	177.7 (1)
Cl(4)-V(1)-O(11)	176.3 (1)	O(21)-V(2)-O(26)	89.8 (1)
Cl(4)-V(1)-O(16)	92.5 (1)	O(21)-V(2)-O(31)	86.5 (1)
Cl(5)-V(1)-O(6)	94.6 (1)	O(26)-V(2)-O(31)	87.2 (1)
Cl(5)-V(1)-O(11)	90.1 (1)	V(1)-Cl(3)-V(2)	73.6 (0)
Cl(5)-V(1)-O(16)	177.7 (1)	V(1)-Cl(4)-V(2)	73.8 (0)
O(6)-V(1)-O(11)	88.1 (1)	V(1)-Cl(5)-V(2)	74.0 (0)
O(6)-V(1)-O(16)	87.6 (1)	Zn-Cl(38)-Zn	87.4 (0)

cm⁻¹ (ϵ , L mol⁻¹ cm⁻¹): 10.0 (m, $\epsilon = 10$), 15.6 (m, $\epsilon = 7$), 22.7 (sh, $\epsilon = 8$), 24.5 (m, $\epsilon = 20$), 25.2 (sh, $\epsilon = 11$), 27.4 (sh, $\epsilon = 8$). Duplication of the synthesis in ref 2 yields a material whose X-ray powder pattern is identical with that of the material produced at 25 °C and to the powder pattern calculated from the single-crystal study.

Magnetic Measurements. Magnetic susceptibilities of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ were determined between 30–250 K and are listed in Table I. The susceptibility expression for antiferromagnetic coupling between two d³, V²⁺ ions is given by

$$\chi_{mol} = \frac{N\beta^2g^2}{3kT} \left[\frac{42 + 15 \exp(6x) + 3 \exp(10x)}{7 + 5 \exp(6x) + 3 \exp(10x) + \exp(12x)} \right]$$

where $x = -J/kT$.¹² The best fit was obtained for $J = -75$ cm⁻¹ and $g = 2.0$.

X-ray Crystallography. A single crystal was cleaved into a nearly equidimensional cube in a dry-nitrogen atmosphere and transferred to a goniostat where it was cooled to -160 °C. A systematic search of a limited hemisphere of reciprocal space revealed no systematic absences or symmetry, indicating a triclinic space group. This was later confirmed by successful solution and refinement. Parameters of the data collection and refinement are shown in Table II. The structure was solved by a combination of direct methods (MULTAN 78) and Fourier techniques and refined by full-matrix least-squares methods. No absorption correction was applied. A final difference Fourier was featureless, the largest peak being 0.45 e/Å³. The results of the structural study are shown in Tables III–V and Figures 1 and 2.

Results and Discussion

Synthesis. Room-temperature reduction of $VCl_3 \cdot 3THF$ with Zn powder in THF leads reproducibly to high yields of a compound of empirical formula $2VCl_2 \cdot ZnCl_2 \cdot 6THF$ in which, as is shown by the X-ray diffraction study, the cation $[V_2(\mu-Cl)_3(THF)_6]^+$ and the anion $[Zn_2(\mu-Cl)_2Cl_4]^{2-}$ are present in a 2:1 ratio.

The formation of the dinuclear cation $[V_2Cl_3(THF)_6]^+$ is not limited to the system $VCl_3 \cdot 3THF/Zn$, but the combination of $VCl_3 \cdot 3THF$ with other metals, e.g. Cd, Sn, Al, Ga, Fe, and

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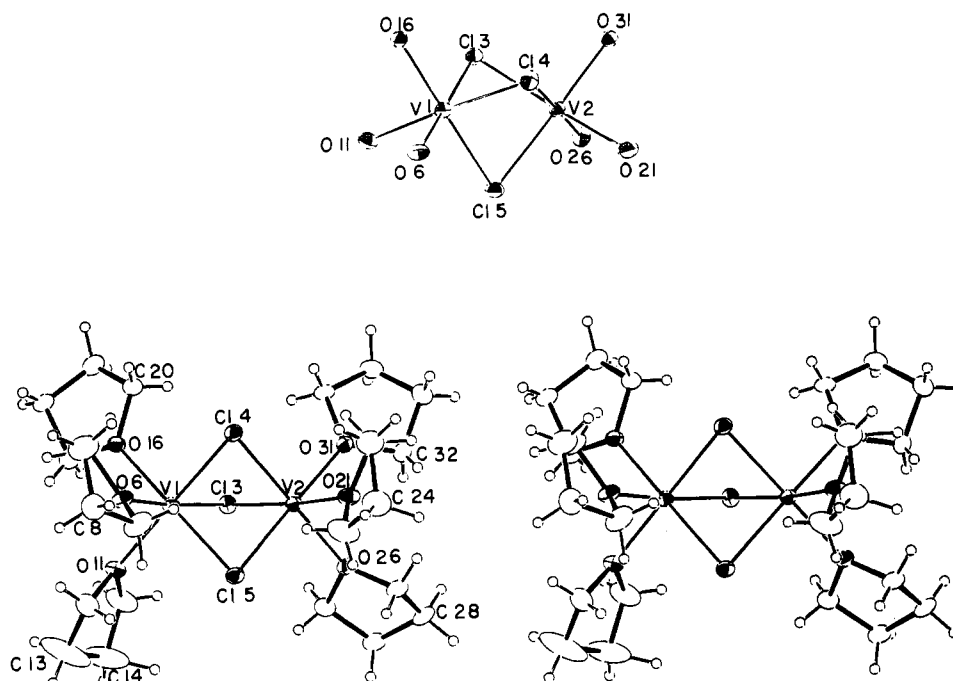


Figure 1. Views of the inner coordination sphere (above) and the full ion $V_2Cl_3(OC_4H_8)_6^+$ (in stereo), showing atom labeling. Unlabeled carbon atoms follow the sequence indicated.

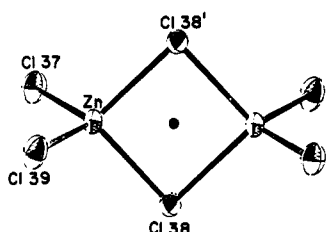


Figure 2. ORTEP drawing of the $Zn_2Cl_6^{2-}$ ion. The symmetry center is shown as a solid dot.

Mn, leads to complexes in which the $[V_3Cl_3(THF)_6]^+$ cation is present.¹³ With more strongly reducing metals, e.g. Mg or Na, the reduction proceeds beyond the V(II) stage and complicated and highly reactive mixtures, possibly containing V(I) and V(0), are formed similar to those reported by Sobota for the systems $VCl_3/M/THF$ ($M = Mg, Na$).¹⁴ We cannot agree with the identification "VCl₂·2THF" for the product from VCl_3 and Zn in boiling THF;² instead, the product is identical (X-ray powder pattern) with that formed by reduction at 25 °C, $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$. The product of zinc reduction of $VCl_3 \cdot 3THF$ in THF, speculated by Köhler et al.¹ to be a mixture of $VCl_2 \cdot 2THF$ and $ZnCl_2 \cdot xTHF$, is in fact the pale green ionic solid we report here. That $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ has been made but not recognized as such can be inferred from a paper by Jacob et al.,¹⁵ who obtained a green crystalline product, formulated as $2VCl_2 \cdot ZnCl_2 \cdot 6THF$, after complex workup of the reaction of VCl_4 with dimethylzinc. It is worth noting that the claimed production of $VCl_2 \cdot 2THF$ from VCl_3 and $LiAlH_4$ ¹⁶ may be equally complex. Separation of $VCl_2 \cdot nL$ from the ionic material $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ by adding ligands L is not a real possibility. With a number of potential ligands, e.g. acetone, Ph_3PO , RNC ($R = tert\text{-butyl}, 2,6\text{-xylyl}$), only substitution of the THF ligands was observed while the ionic complex as such

remained intact. With other ligands (e.g. amines, pyridine, triethylphosphine) indeed formation of $VCl_2 \cdot nL$ took place, but it was very difficult to separate this from the $ZnCl_2 \cdot xL$ that was formed simultaneously. If $VCl_2 \cdot nL$ is desired, the electrochemical synthesis should be used.^{17,18}

The ionic complex, $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$, is however an excellent starting material for a number of organometallic V(II) compounds, e.g. Cp_2V ,¹ Cp^*_2V ,¹³ and bis(fulvalene)-divanadium.³ In other reactions the Zn remains in the products, leading to novel mixed V–Zn compounds. In this respect we mention reaction of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ with $LiBH_4$ in the presence of phosphines to give the bimetallic zinc–vanadium polyhydride, $V_2Zn_2H_4(BH_4)_2(PMePh_2)_4$.⁶

Molecular Structure and Physical Properties. The results of an X-ray diffraction study are presented in Tables II–V and Figures 1 and 2. The crystals are composed of $[V_2(\mu\text{-Cl})_3(THF)_6]^+$ cations and $[Zn_2(\mu\text{-Cl})_2Cl_4]^{2-}$ anions in a 2:1 ratio. The cation is composed of two *fac*- VCl_3O_3 octahedra sharing a Cl_3 triangular face (Figure 1), while the anion is composed of two $ZnCl_4$ tetrahedra sharing an edge (Figure 2). The $Zn_2Cl_6^{2-}$ ion possesses a crystallographic center of symmetry, but this anion has effective D_{2h} symmetry.¹⁹ The *fac*- VCl_3O_3 unit maintains a close approximation to local octahedral symmetry. O–V–O angles range from 86.5 to 89.8° while Cl–V–Cl angles range from 87.3 to 88.0°. Only one lone pair of each THF appears to donate to V, since every oxygen is pyramidal.²⁰ Oxygen atoms lie out of their respective attached VCC plane by 0.25–0.95 Å. The V–O distances in $V_2Cl_3(THF)_6^+$ (average value 2.143 Å) are close to those in $[V(THF)_4][V(CO)_6]_2$ (2.17 Å).²¹ The V–(μ-Cl) distances in this cation (average value 2.477 Å) are, surprisingly, only minutely longer than that (2.46 Å) to terminal chlorine in *trans*- $VCl_2(py)_4$.²² For comparison, the V–Cl distance in $CpVCl_2(PMe_3)_2$ is 2.40 Å.²³

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Table VI. Structural Parameters of the $M_2(\mu\text{-Cl})_3$ Unit

	$R(M-M)$, Å	$\angle(M-Cl-M)$, deg	$R(M-Cl)$, Å	ref
$Ti_2Cl_9^{3-}$	3.43	86.7	2.493	a
$V_2Cl_3(THF)_6^+$	2.97	73.8	2.477	this work
$Cr_2Cl_9^{3-}$	3.12	76.4	2.52	b

a Kirstenmacher, T. J.; Stucky, G. D. *Inorg. Chem.* 1971, 10, 122. b Wessel, G. J.; Ijdo, D. J. W. *Acta Crystallogr.* 1957, 10, 4661.

Whereas there is no direct V-V bonding in the d^2-d^2 dimer $[CpV(O_2CR)_2]_2$ ($V\cdots V \cong 3.7$ Å),^{24,25} there are structural symptoms of incipient V-V bonding in $[V_2Cl_3(THF)_6]^+$. Thus, while the observed V-V distance of 2.97 Å is much longer than the 2.73 Å in $V_2(CO)_8(\mu\text{-PMe}_2)_2$,²⁶ the 2.46 Å in $Cp_2V_2(CO)_5$,²⁷ the 2.439 Å in $Cp_2V_2(C_8H_8)_5$,⁵ and the 2.20 Å in $V_2[C_6H_3(OMe)_2]_4$,²⁸ it is shorter than the 3.255 Å in $[CpV(\mu\text{-Cl})PEt_3]_2$.²⁹ A useful standard for comparison is the set of isostructural face-shared octahedra listed in Table VI. The metal-metal separation in the d^0-d^0 dimer $[Ti_2Cl_9]^-$ is nearly 0.5 Å longer than in the d^3-d^3 species $[V_2Cl_3(THF)_6]^+$. Perhaps the most revealing comparison is with the d^3-d^3 dimer $Cr_2Cl_9^{3-}$, which has a longer M-M distance in spite of the fact that Cr(III) is inherently smaller than V(II). The contracted V-V distance suggests some bonding interaction between the metal atoms, which may be expected to manifest itself as magnetic coupling between the two d^3 centers. Antiferromagnetism is indeed observed, with an exchange integral ($-J = 75$ cm⁻¹, calculated from the magnetic susceptibility between 30 and 270 K; Table I) considerably larger than in the iso-electronic $Cr_2Cl_6^{3-}$ systems³⁰ ($-J$ varies with the counterion between 4 and 11 cm⁻¹). A smaller exchange integral ($-J = 40$ cm⁻¹) is also found for $[Et_3N]_3[V_2Cl_6]$, a V(III) complex anion with three halogen bridges.³¹ In the V(II) complex the metal orbitals are larger and can give a better overlap, leading to a stronger magnetic interaction and the observed increase in the exchange integral, $-J$. For $[CpV(\mu\text{-Cl})PEt_3]_2$ ($V-V = 3.255$ Å²⁹), the exchange integral ($-J = 110$ cm⁻¹) is considerably larger, despite the fact that the distance between the metal centers is 0.3 Å longer. In the V(III) carboxylates, $[CpV(O_2CR)_2]_2$, the exchange between the d^2 centers is even stronger ($-J$ varies between 110 and 165 cm⁻¹, depending on R³²), despite the fact that the V-V distance (3.63-3.70 Å)^{24,25} is 0.6 Å larger than twice the covalent radius of vanadium. Strong superexchange through the four bridging carboxylate ligands was suggested as a mechanism for this unusually strong magnetic interaction.^{25,32}

The electronic spectrum of the $[V_2Cl_3(THF)_6]^+$ cation in CH_2Cl_2/THF (340-1200 nm) is typical of spin-allowed, Laporte-forbidden transitions. The spectrum is remarkably similar to that reported for authentic (from electrochemical reduction) $VCl_2 \cdot 2THF$ in THF.¹⁸ This, taken with the observed antiferromagnetic for the latter,¹⁸ leads us to suggest for authentic $VCl_2 \cdot 2THF$ in solution a structure similar to the one

reported here, e.g. $[V_2Cl_3(THF)_6]Cl$. When the observed spectrum is idealized to V(II) in an octahedral ligand field, the maxima are assigned as ${}^4A_{2g} \rightarrow {}^4T_{2g}$ ($\nu = 10.0 \times 10^3$ cm⁻¹), ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ ($\nu = 15.6 \times 10^3$ cm⁻¹), and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ ($\nu = 24.5 \times 10^3$ cm⁻¹). From these data, values for $10Dq$ (10.0×10^3 cm⁻¹) and the electron repulsion parameter, B (814 cm⁻¹), can be calculated.³³ These predict ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ at 26.2×10^3 cm⁻¹. The actual local symmetry (C_{3v}) is evident as shoulders in the high-energy band due to splitting of the $T_{1g}(P)$ level, while the lower energy bands are too broad ($\Delta\nu_{1/2} = (2-3) \times 10^3$ cm⁻¹) for normal high-symmetry d-d transitions.

Conclusions. The precipitated solid from the zinc reduction of $VCl_3 \cdot 3THF$ has precisely the average solution composition resulting from this one-electron reduction: $VCl_2 \cdot 1/2 ZnCl_2 \cdot 3THF$. The isolation of this unexpectedly complicated product is probably due more to its low solubility than to its exceptional stability. Spin coupling within the two d^3 centers in the cation is significant compared to analogous systems, but nevertheless only comparable to thermal energies in the range 100-300 K and thus weaker than, for example, a hydrogen bond. At the same time, this weak interaction is in part responsible for the dimeric aggregation that is proposed to facilitate multielectron reduction of N_2 by V(II), thereby avoiding high-energy or radical nitrogenous intermediates.⁷

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Registry No. $[V_2(\mu\text{-Cl})_3(THF)_6]_2[Zn_2Cl_6]$, 90823-11-3; $VCl_3 \cdot 3THF$, 19559-06-9; Zn, 7440-66-6.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen positional and thermal parameters, C-C and C-O distances, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Thionitrosyl and Bridging Sulfide Complexes of Dicarboxyl[hydridotris(3,5-dimethylpyrazolyl)borato]metal (Metal = Molybdenum and Tungsten)

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The few transition-metal-thionitrosyl complexes that are known have displayed some remarkable chemical and physical properties in relation to those of their more common metal-nitrosyl analogues.¹⁻⁸ There is considerable interest in ex-

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