Preparation, Crystal Structure and Magnetochemistry of $[NEt_4][V_2Cl_7(thf)_2]\cdot CH_2Cl_2$ (thf = tetrahydrofuran)†

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The reaction between $[VCl_3(thf)_3]$ and $[NEt_4]_2[VOCl_4]$ resulted in Cl^- transfer from the $[VO]^{2+}$ reagent and the formation of anionic V^{III} products. In MeCN solution, the product was the known $[NEt_4][VCl_4(MeCN)_2]$, whereas in CH_2Cl_2 solution the new complex $[NEt_4][V_2Cl_7(thf)_2]\cdot CH_2Cl_2$ **4** was obtained. The structure of the anion of **4** consists of a face-sharing bioctahedron with three μ-Cl^- ions. The V$\cdots$V distance of 3.176(2) Å precludes metal–metal bonding. Variable-temperature magnetic susceptibility (χ_m) studies on solid samples of **4** in the temperature range 5.0–300 K have been performed. The data were satisfactorily fitted to the theoretical χ_m *vs.* T expression for a d^2–d^2 dinuclear complex. The fitting parameters obtained were $J = -48(1)$ cm^{-1} ($\hat{H} = -2JS_1\cdot S_2$), $g = 1.90$ and a 4.1% paramagnetic impurity. The V^{III} ions are thus antiferromagnetically coupled.

We are engaged in a research programme directed towards the development of certain aspects of the chemistry of vanadium with oxygen and/or sulfur ligation. This work is stimulated by the relevance of this area to vanadium involvement in crude oil hydrotreating processes; crude oil vanadyl impurities are reduced and transformed to sulfides under processing conditions, ultimately to insoluble vanadium sulfides (primarily V_2S_3 and V_3S_4), which deposit on and poison the supported molybdenum hydrodesulfurization catalyst.[1-3] We have been preparing a number of vanadium species of various nuclearities and oxidation levels.[4,5] In many cases, these complexes have been paramagnetic and have involved magnetic exchange interactions between the constituent V^{III} and/or V^{IV} ions. As a result, we have sought to characterize these interactions *via* magnetochemical methods. It is particularly relevant to this work to note that, in contrast to, *e.g.*, Cu^{II} systems, relatively few dinuclear V^{III} (or V^{IV}) systems have been magnetochemically characterized; a contributing factor to this is undoubtedly the usual air- and moisture-sensitivity of V^{III} systems, and the tendency of $[VO]^{2+}$ complexes to be mononuclear.

In this paper, we describe a product obtained from the reaction between $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) and $[VOCl_4]^{2-}$. We have shown earlier[6] that this reaction in a 3:1 ratio in MeCN, and in the presence of $Na_2(edt)$ (H_2edt = ethane-1,2-dithiol) and a reducing agent leads to the formation of the V^{III} complex $[V_4O(edt)_2Cl_8]^{2-}$. To assist in understanding this transformation (and others currently being investigated), it was important to determine the product of the reaction between $[VCl_3(thf)_3]$ and $[VOCl_4]^{2-}$ alone. For example, oxo-bridged $V^{III}V^{IV}$ mixed-valence species were considered to be one type of possible product. In fact we have now established that the reaction between $[VCl_3(thf)_3]$ and $[VOCl_4]^{2-}$ leads to Cl^- ion transfer and the formation of the V^{III} species $[VCl_4(MeCN)_2]^-$ or $[V_2Cl_7(thf)_2]^-$ in MeCN or CH_2Cl_2, respectively. We herein describe these results in detail, together with a variable-temperature magnetochemical study of the latter complex.

Experimental

General.—All manipulations were carried out under anaerobic conditions (dinitrogen atmosphere) employing standard Schlenk and dry-box techniques. Acetonitrile and CH_2Cl_2 were purified by distillation from CaH_2; Et_2O and hexanes were purified by distillation from sodium–benzophenone. The complexes $[VCl_3(thf)_3]$ **1**[7] and $[NEt_4]_2[VOCl_4]$ **2**[8,9] were prepared as described elsewhere.

Reaction of Complexes **1** *and* **2** *in* MeCN.—Acetonitrile (20 cm^3) was added to a mixture of $[VCl_3(thf)_3]$ (0.374 g, 1.00 mmol) and $[NEt_4]_2[VOCl_4]$ (0.469 g, 1.00 mmol). The solids dissolved on stirring to give a green solution, which deposited a fine yellow powder. The slurry was stirred until the reaction appeared complete, and then filtered. The yellow precipitate of $[NEt_4][VCl_4(MeCN)_2]$ **3** was washed with MeCN and dried *in vacuo*. Yield: 0.38 g (94% based on initial V^{III}) (Found: C, 35.0; H, 6.3; Cl, 34.2; N, 10.1. $C_{12}H_{26}Cl_4N_3V$ requires C, 35.6; H, 6.5; Cl, 35.0; N, 10.4%).

The green filtrate and washings were reduced in volume under vacuum and the flask stored at −10 °C. After a few days the resulting green crystals were collected by filtration and dried *in vacuo*. The crystals analysed for the formula $[NEt_4][VOCl_3(MeCN)_{0.5}(H_2O)_{1.5}]$ (Found: C, 30.4; H, 7.5; Cl, 30.9; V, 15.1. $C_9H_{24.5}Cl_3N_{1.5}O_{2.5}V$ requires C, 30.8; H, 7.0; Cl, 30.3; V, 14.5%). Infrared (Nujol): 992 cm^{-1} (VO^{2+}).

Reaction of Complexes **1** *and* **2** *in* CH_2Cl_2.—Dichloromethane (20 cm^3) was added to a mixture of $[VCl_3(thf)_3]$ (0.560 g, 1.50 mmol) and $[NEt_4]_2[VOCl_4]$ (0.235 g, 0.500 mmol). The solids dissolved to give a deep red solution. After several minutes, the solution was filtered and the filtrate layered with hexanes (5 cm^3). Extremely long (> 1 cm) red needles slowly formed over several days, and were collected by filtration. They were found suitable for crystallography and identified as $[NEt_4][V_2Cl_7(thf)_2]\cdot CH_2Cl_2$ **4**. Yield 0.33 g (63% based on V^{III}).

Rational Synthesis of $[NEt_4][V_2Cl_7(thf)_2]\cdot CH_2Cl_2$ **4**.—Dichloromethane (40 cm^3) was added to a mixture of $[VCl_3(thf)_3]$ (3.74 g, 10.0 mmol) and 'anhydrous' NEt_4Cl (0.83 g, 5.0 mmol). The solids dissolved with stirring to produce a clear deep red solution. This was filtered and the filtrate layered with hexanes (40 cm^3). After several days, long red needles were collected by filtration. Yield: 2.81 g (80%). The analytical data indicated a formulation $[NEt_4][V_2Cl_7(thf)_2]\cdot CH_2Cl_2\cdot H_2O$, the water presumably originating from the NEt_4Cl (Found: C,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Crystallographic data for $[NEt_4][V_2Cl_7(thf)_2]\cdot CH_2Cl_2$ **4**

Formula[a]	$C_{17}H_{38}Cl_9NO_2V_2$
M	709.45
Space group	$P\bar{1}$
Crystal size/mm	0.15 × 0.25 × 0.40
a/Å	11.946(4)
b/Å	14.277(4)
c/Å	9.337(3)
α/°	93.83(1)
β/°	110.55(1)
γ/°	88.80(2)
U/Å^3	1487.9
Z	2
T/°C	−145
Radiation[b]	Mo-Kα (λ 0.710 69 Å)
D_c/g cm^{-3}	1.584
μ/cm^{-1}	14.413
Octants	$+h, \pm k, \pm l$
Total data	3939 ($6 \leqslant 2\theta \leqslant 45°$)
Unique data	3883
Observed data [$F > 3\sigma(F)$]	3230
$R(R')$[c,d]	0.0540 (0.0562)

[a] Including solvate molecule. [b] Graphite monochromator. [c] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [d] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w = 1/\sigma^2(|F_o|)$.

28.0; H, 5.2; N, 1.8; V, 13.6. $C_{17}H_{40}Cl_9NO_3V_2$ requires C, 28.1; H, 5.5; N, 1.9; V, 14.0%).

Preparation of $[NEt_4]_3[V_2Cl_9]$ **5**.—Dichloromethane (25 cm^3) was added to a mixture of $[VCl_3(thf)_3]$ (0.374 g, 1.00 mmol) and 'anhydrous' NEt_4Cl (0.25 g, 1.5 mmol). The slurry was stirred overnight, after which the flask contained a deep violet microcrystalline precipitate and a virtually colourless mother-liquor. The solid was collected by filtration, washed with CH_2Cl_2, and dried *in vacuo*. The yield was essentially quantitative (Found: C, 34.8; H, 7.0; N, 5.5. $C_{24}H_{60}Cl_9N_3V_2$ requires C, 35.5; H, 7.4; N, 5.2%).

Conversion of $[NEt_4][V_2Cl_7(thf)_2]$ *to* $[NEt_4][VCl_4(MeCN)_2]$.—A stirred slurry of complex **4** (0.71 g, 1.0 mmol) in MeCN (20 cm^3) slowly leads to dissolution of the red needles and the appearance of a yellow powder. The latter was collected by filtration and identified as **3** by spectroscopic comparison with authentic material. Yield: 0.36 g (45% based on V^{III} but 89% based on NEt_4^+). Addition of NEt_4Cl (0.17 g, 1.0 mmol) to the filtrate produced a second crop of yellow powder in equal amount, bringing the total yield to 90% based on V^{III}. A reaction performed with the NEt_4Cl added initially led to a comparable yield of **3**.

Crystal-structure Analysis of Compound **4**.—Data were collected on a Picker four-circle diffractometer by using standard low-temperature facilities; details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.[10] Data collection and structure solution information are listed in Table 1. The structure was solved by a combination of direct methods (MULTAN78[11]) and Fourier techniques and refined by full-matrix least-squares methods.

A systematic search of a limited hemisphere of reciprocal space revealed no symmetry or systematic absences. The initial choice of space group $P\bar{1}$ was later proven correct by the successful solution and refinement of the structure. After the non-hydrogen atoms had been located and partially refined, an attempt to locate the hydrogen atoms in a Fourier difference map phased on the non-hydrogen atoms was not very successful. The hydrogen atoms were, however, included in fixed, calculated positions to improve the refinement of the non-hydrogen atoms. In the final cycles of least-squares refinement the non-hydrogen atoms were refined with anisotropic thermal parameters. The final difference Fourier map was essentially featureless, the largest residual peak being 0.89 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Other Measurements.—Variable-temperature magnetic susceptibility measurements were made on a Quantum Design MPMS SQUID susceptometer at Michigan State University. Measurements were made with an applied magnetic field of 0.1 T (1000 G) in the temperature range 5.0–300.0 K. The sample size was 0.0670 g. A diamagnetic correction factor of -434.63×10^{-6} cm^3 mol^{-1} was estimated using Pascal's constants and subtracted from the experimental data to yield the molar paramagnetic susceptibility of the compound. The data were then fitted to the appropriate theoretical expression for the χ_M *vs.* *T* behaviour of a d^2–d^2 dinuclear species, using a least-squares fitting procedure.[12]

IR spectra were recorded on a Perkin-Elmer 283 or a Nicolet 510P FTIR spectrophotometer as Nujol mulls on CsI plates. Elemental analyses were performed by Oneida Research Services or by the Microanalytical Laboratory of the University of Manchester.

Results and Discussion

Syntheses.—As stated above, we were interested in determining whether reactions between $[VCl_3(thf)_3]$ **1** and $[NEt_4]_2[VOCl_4]$ **2** lead to mixed-valence, oxo-bridged species. A number of ratios of **1**:**2** in MeCN were explored; all gave a yellow precipitate and a green solution. The yellow solid was identified by elemental analysis and IR spectroscopy to be the known $[NEt_4][VCl_4(MeCN)_2]$ **3**.[13] Cooling of the filtrate gave a green microcrystalline solid with an IR band at 992 cm^{-1} assignable to a $[VO]^{2+}$ unit, and a formula by elemental analysis of $[NEt_4][VOCl_3(solv)_2]$ (solv = MeCN and/or H_2O). The reaction is concluded to have involved Cl^- ion transfer from $[VOCl_4]^{2-}$ to $[VCl_3(thf)_3]$, as summarized in equation (1). The yield of **3** based on available V^{III} is essentially quantitative provided the $[VOCl_4]^{2-}$:$[VCl_3(thf)_3]$ ratio is ⩾1:1; when ratios of <1:1 are employed, the yield is correspondingly decreased, suggesting that each $[VOCl_4]^{2-}$ unit can only transfer one Cl^- ion. The green '$[VOCl_3(solv)_2]^-$' product ion in the 1:1 reaction could be either mononuclear or of higher nuclearity. The $[VO]^{2+}$ stretching frequency is too high for there to be a ligand bound *trans* to the multiply bonded oxygen atom, and the product therefore is most likely $[NEt_4][VOCl_3(solv)]\cdot solv$ or $[NEt_4]_2[V_2O_2Cl_6]\cdot 2solv$ with square-pyramidal V^{IV} centres; the $[V_2O_2Cl_6]^{2-}$ ion with two μ-Cl^- ions is known in the literature.[14]

$$[VOCl_4]^{2-} + VCl_3 \xrightarrow{MeCN} [VOCl_3]^- + [VCl_4(MeCN)_2]^- \quad (1)$$

The reactions between **1** and **2** in MeCN obviously do not involve the $[VO]^{2+}$ group, as judged by the identity of the products, but we wondered whether precipitation of **3** was preventing a mixed-valence, oxo-bridged species from forming. The 1:1 reaction was therefore repeated in a poorly coordinating solvent, namely CH_2Cl_2. No precipitate was obtained from this solvent, but unfortunately it proved difficult to isolate pure materials for characterization; it did appear, however, that there were at least two or three products. Infrared spectra invariably showed strong peaks assignable to $[VO]^{2+}$ stretches, suggesting that at least some, if not all, of the $[VO]^{2+}$ units of **2** were remaining unchanged. Variation of the **1**:**2** reaction ratio was then explored, and the 3:1 ratio was found to lead to a characterizable product. Addition of hexanes to the deep red solution produced long, dark-red crystals of a complex identified as $[NEt_4]_2[V_2Cl_7(thf)_2]\cdot CH_2Cl_2$ **4**, a V^{III} species. The yield of **4** was 60–65% based on available V^{III}; this is consistent with $[VOCl_4]^{2-}$ again only transferring one Cl^- ion, as summarized in equation (2) which predicts a 67% yield

$$3[VCl_3(thf)_3] + [VOCl_4]^{2-} \longrightarrow [V_2Cl_7(thf)_2]^- + \text{`}[VOCl_3]\text{'} + [VCl_3(thf)_3] \quad (2)$$

of **4**. Solid isolated from the filtrate showed a strong $[VO]^{2+}$ stretch in the IR spectrum, suggesting again that only Cl^- ion transfer has occurred.

Once complex **4** was identified as a new compound, a rational and convenient synthesis of large quantities was sought and developed. High yields (≈80%) of pure material were obtained by treatment of **1** with 0.5 equivalents of NEt_4Cl in CH_2Cl_2, as summarized in equation (3). Increasing the amount of NEt_4Cl

$$2[VCl_3(thf)_3] + NEt_4Cl \longrightarrow [NEt_4][V_2Cl_7(thf)_2] + 4\,thf \quad (3)$$

to 1.5 equivalents provided an equally convenient route to $[NEt_4]_3[V_2Cl_9]$ **5**, equation (4).

$$2[VCl_3(thf)_3] + 3\,NEt_4Cl \longrightarrow [NEt_4]_3[V_2Cl_9] \quad (4)$$

Finally, it was clear that the difference in product identity for the MeCN and CH_2Cl_2 reactions was due to the different donor properties of the two solvents, and that **4** was thus likely to be unstable in MeCN. This was confirmed by dissolution of the red complex **4** in MeCN, which was followed by rapid precipitation of the yellow complex **3**. In the presence of added Cl^-, the yield is essentially quantitative, according to equation (5).

$$[V_2Cl_7(thf)_2]^- + Cl^- \xrightarrow{MeCN} 2[VCl_4(MeCN)_2]^- + 2\,thf \quad (5)$$

Description of the Structure of Compound **4**.—An ORTEP[15] representation of the anion of complex **4** is provided in Fig. 1. Atomic coordinates and selected bond distances and angles are listed in Tables 2 and 3, respectively. The asymmetric unit contains one anion, one cation and one CH_2Cl_2 molecule with the former possessing no imposed symmetry; the latter two will not be discussed further. The structure of the anion is a face-sharing bioctahedron with a V(1) ··· V(2) distance of 3.176(2) Å, which is too long for direct metal–metal bonding. All bridging and terminal sites are occupied by Cl^- ions except for one site on each metal which is occupied by a thf molecule; the resulting structure has idealized C_2 symmetry. Interestingly, O(10) and O(15) are trigonal planar rather than pyramidal, the sum-of-angles at O(10) and O(15) both being 359.9°. Further, the two thf rings are approximately coplanar, as can be seen in the side-view in Fig. 1. The above structural features can be rationalized as due to the steric bulk of the adjacent Cl^- ions, as emphasized by the space-filling diagram in Fig. 1.

The anion of **4** has unexceptional bond distances and angles when compared with other $(\mu\text{-}Cl)_3$-bridged bioctahedral structures such as $Cs_2[Cr_2Cl_9]$ (Cr ··· Cr 3.12 Å)[16] and $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ [V ··· V 2.973(1) Å][17] containing Cr^{III} and V^{II}, respectively. The calculated M–(μ-Cl)–M angle in a regular confacial bioctahedral is 70.5°. This angle in the above complexes is 76.6 or 74.4°, respectively, and in **4** it is 80.9°, all consistent with repulsive interactions between the positively charged metal centres. Greater repulsion between the V^{3+} ions in **4** compared with the V^{2+} ions in $[V_2Cl_3(thf)_6]^+$ also rationalizes the greater bridge angle in the former *versus* the latter.

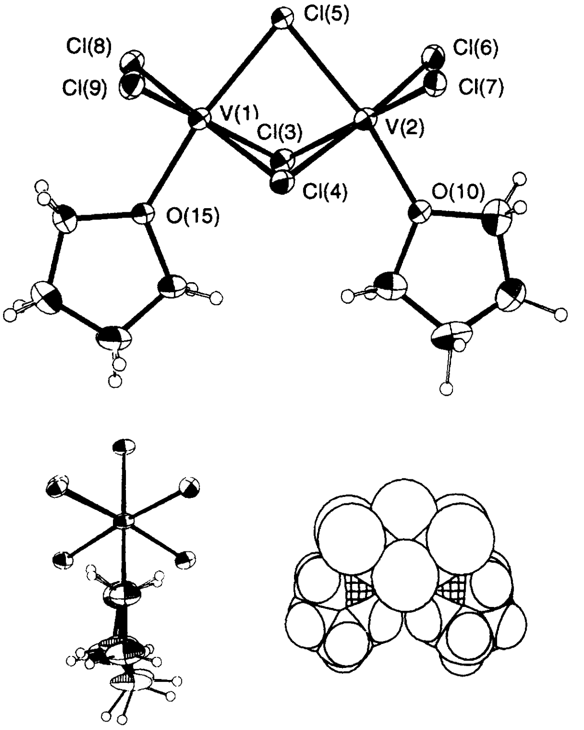

Fig. 1 ORTEP representation of the anion of complex **4**. Thermal ellipsoids are at the 50% probability level except for the hydrogen atoms, which are of arbitrary size. On the bottom right is shown a space-filling diagram, and on the bottom left a view along the V–V vector

Table 2 Atomic coordinates* for $[NEt_4][V_2Cl_7(thf)]\cdot CH_2Cl_2$ **4**

Atom	*x*	*y*	*z*
V(1)	9 665(1)	2 750(1)	7 288(1)
V(2)	12 256(1)	3 666(1)	8 547(1)
Cl(3)	10 566(1)	3 915(1)	9 403(2)
Cl(4)	10 651(1)	3 754(1)	6 048(2)
Cl(5)	11 647(1)	2 022(1)	8 251(2)
Cl(6)	13 594(1)	3 535(1)	11 032(2)
Cl(7)	13 705(1)	3 407(1)	7 435(2)
Cl(8)	8 884(1)	1 939(1)	8 763(2)
Cl(9)	8 987(2)	1 755(1)	5 137(2)
O(10)	12 477(4)	5 069(3)	8 677(5)
C(11)	13 626(8)	5 560(6)	9 281(12)
C(12)	13 301(9)	6 575(6)	9 370(15)
C(13)	12 171(9)	6 655(6)	8 163(12)
C(14)	11 522(8)	5 784(6)	8 239(11)
O(15)	8 156(4)	3 563(3)	6 550(5)
C(16)	8 107(7)	4 594(5)	6 646(12)
C(17)	6 890(8)	4 845(6)	5 725(12)
C(18)	6 128(7)	4 025(6)	5 521(13)
C(19)	6 934(6)	3 202(5)	5 914(10)
N(20)	2 110(5)	1 193(4)	3 378(6)
C(21)	2 513(6)	601(5)	4 754(8)
C(22)	3 196(7)	−278(5)	4 574(9)
C(23)	3 133(7)	1 427(5)	2 883(8)
C(24)	4 149(7)	1 963(5)	4 065(9)
C(25)	1 575(6)	2 086(5)	3 882(8)
C(26)	1 150(7)	2 789(5)	2 669(9)
C(27)	1 171(7)	671(5)	2 018(8)
C(28)	38(7)	423(5)	2 234(9)
C(29)	4 877(8)	1 307(6)	9 587(11)
Cl(30)	5 568(2)	1 097(2)	8 232(3)
Cl(31)	5 899(3)	1 160(2)	11 445(3)

* × 10^4. Numbers in parentheses are estimated standard deviations on the least significant figure.

Table 3 Selected interatomic distances (Å) and angles (°) for $[NEt_4][V_2Cl_7(thf)_2]\cdot CH_2Cl_2$ (**4**)

V(1) ··· V(2)	3.176(2)	V(1)–O(15)	2.053(5)
V(1)–Cl(3)	2.443(2)	V(2)–Cl(3)	2.430(2)
V(1)–Cl(4)	2.457(2)	V(2)–Cl(4)	2.454(2)
V(1)–Cl(5)	2.454(2)	V(2)–Cl(5)	2.441(2)
V(1)–Cl(8)	2.295(2)	V(2)–Cl(6)	2.328(2)
V(1)–Cl(9)	2.286(2)	V(2)–Cl(7)	2.323(2)
		V(2)–O(10)	2.016(5)
Cl(3)–V(1)–Cl(4)	80.40(7)	Cl(3)–V(2)–Cl(5)	83.72(7)
Cl(3)–V(1)–Cl(5)	83.16(7)	Cl(3)–V(2)–Cl(6)	92.72(8)
Cl(3)–V(1)–Cl(8)	91.46(8)	Cl(3)–V(2)–Cl(7)	173.18(8)
Cl(3)–V(1)–Cl(9)	171.68(8)	Cl(3)–V(2)–O(10)	88.89(15)
Cl(3)–V(1)–O(15)	89.72(14)	Cl(4)–V(2)–Cl(5)	83.36(7)
Cl(4)–V(1)–Cl(5)	83.03(7)	Cl(4)–V(2)–Cl(6)	172.94(8)
Cl(4)–V(1)–Cl(8)	171.79(8)	Cl(4)–V(2)–Cl(7)	92.53(8)
Cl(4)–V(1)–Cl(9)	91.43(8)	Cl(4)–V(2)–O(10)	90.12(14)
Cl(4)–V(1)–O(15)	89.78(14)	Cl(5)–V(2)–Cl(6)	93.38(7)
Cl(5)–V(1)–Cl(8)	95.00(7)	Cl(5)–V(2)–Cl(7)	94.54(7)
Cl(5)–V(1)–Cl(9)	94.38(7)	Cl(5)–V(2)–O(10)	170.84(15)
Cl(5)–V(1)–O(15)	170.61(14)	Cl(6)–V(2)–Cl(7)	93.97(8)
Cl(8)–V(1)–Cl(9)	96.68(8)	Cl(6)–V(2)–O(10)	92.38(15)
Cl(8)–V(1)–O(15)	91.28(15)	Cl(7)–V(2)–O(10)	92.16(15)
Cl(9)–V(1)–O(15)	91.81(14)	V(1)–Cl(3)–V(2)	81.34(7)
Cl(3)–V(2)–Cl(4)	80.72(7)	V(1)–Cl(4)–V(2)	80.59(7)
		V(1)–Cl(5)–V(2)	80.91(7)

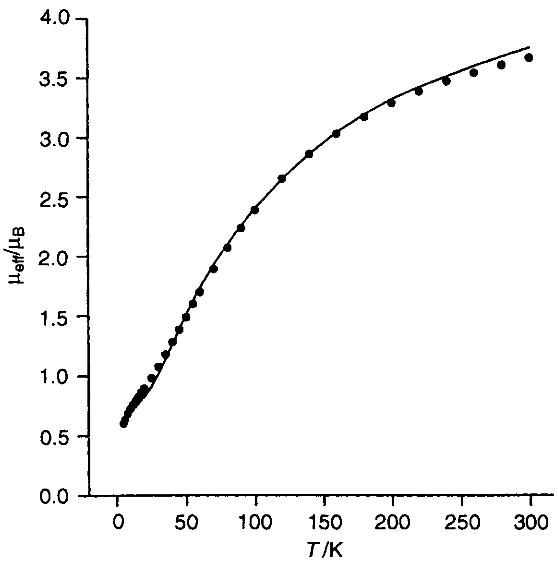

Fig. 2 A plot of the effective magnetic moment (μ_{eff}) *vs.* T for complex **4**. The solid line is a fit of the experimental data to the theoretical expression of equation (7). See the text for the fitting parameters

The above M ··· M distances and M–Cl–M bridge angles are in contrast to those for *syn*-$[Mo_2Cl_7(PMe_3)_2]^-$ (2.69–2.76 Å, 66.3–68.1°)[18] and $[W_2Cl_7(thf)_2]^-$ [2.409(4) Å, 58.4°][19] which possess structures similar to the anion of **4**. The shorter M ··· M separations and acute bridging angles are fully consistent with metal–metal bonding in the Mo^{III} and W^{III} complexes.

Magnetic Susceptibility Studies.—Variable-temperature, solid-state, magnetic susceptibility studies have been performed on powdered samples of $[NEt_4][V_2Cl_7(thf)_2]\cdot CH_2Cl_2$ **4** in the temperature range 5.0–300 K. The effective magnetic moment, μ_{eff}, per V_2 steadily decreased from 3.67 μ_B at 300 K to 0.60 μ_B at 5.0 K. This behaviour is indicative of antiferromagnetic exchange interactions between the V^{III} (d^2) ions; the spin-only μ_{eff} value for a dinuclear complex with non-interacting V^{III} ions is 4.00 μ_B. The χ_m *vs.* T data were fitted to the theoretical expression shown in equation (6) for the χ_m *vs.* T dependence of

$$\chi_m = \frac{(Ng^2\mu_B{}^2/kT)(10e^{6x} + 2e^{2x})}{(5e^{6x} + 3e^{2x} + 1)} \qquad (6)$$

a d^2–d^2 system (derived employing the Heisenberg spin-Hamiltonian $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$) where $x = J/kT$ and the other symbols have their usual meanings. To allow for the presence of a paramagnetic impurity, as indicated by a tail in the experimental χ_m data at low temperatures, the modified equation (7) was, in fact, employed, where ρ = mole fraction of

$$\chi_m{}^{calc} = \chi_m(1 - \rho) + \rho\chi_m{}^{imp} + \text{t.i.p.} \qquad (7)$$

paramagnetic impurity [assumed to be a mononuclear V^{III} ($S = 1$) species], $\chi_m{}^{imp} = 2\ Ng^2\mu_B{}^2/3kT$, and t.i.p. is the temperature-independent paramagnetism. A fit of the experimental data to equation (7) was obtained with $J = -48(1)$ cm^{-1}, $g = 1.90$ and $\rho = 0.041$, with t.i.p. held constant at 200×10^{-6} cm^3 mol^{-1}. The fit is shown as a solid line in Fig. 2, where the data are plotted as μ_{eff} *vs.* T.

It is instructive to compare the value of J determined for complex **4** with other values obtained for $[V_2(\mu\text{-}Cl)_3]^{3+}$ complexes. The exchange interactions within the $[V_2X_9]^{3-}$ (X = Cl or Br) ions have been the topic of several papers.[20–24] In 1968, Casey and Clark[20] examined the magnetic properties of $[NEt_4]_3[V_2Cl_9]$ and found that they could not obtain a good fit for the experimental χ_M *vs.* T data using a theoretical expression derived as for equation (6). The poor agreement between observed and predicted behaviour is due to the assumption inherent in using the Heisenberg Hamiltonian $\hat{H} = -2JS_1\cdot S_2$ that only spin angular momentum is involved. This is normally a good approximation for metal complexes in general and for V^{III} complexes in particular, where the symmetry is low enough as to give an orbitally non-degenerate ground state and a consequent quenching of orbital angular momentum. However, in $[V_2Cl_9]^{3-}$, the distortions from O_h to C_{3v} symmetry at each V^{III} centre are not severe, and the molecule retains orbital angular momentum. From the general profile of the χ_M *vs.* T curve, Casey and Clark estimated a rough value for J of ≈ -40 cm^{-1}. In 1984, Leuenberger and Gudel[22] provided a theoretical treatment for exchange interactions in $[Ti_2X_9]^{3-}$ (X = Cl or Br) which included orbital angular momentum; they still needed to assume high symmetry and to make certain assumptions and simplifications in order to make the problem manageable. Note also that inelastic neutron scattering and magnetic circular dichroism studies on $Cs_3[V_2Cl_9]$ and $Rb_3[V_2Br_9]$ suggest these compounds have *ferro*magnetic exchange interactions.[24]

In contrast to previous problems with $[V_2Cl_9]^{3-}$ and similar complexes with virtual D_{3h} symmetry, the observed χ_M *vs.* T behaviour of complex **4** is well fitted by equation (6) based on the Heisenberg Hamiltonian. As can be seen in Fig. 2, the agreement between the predicted behaviour (solid line) and the experimental points is not perfect throughout the temperature range investigated, but it is nevertheless very good. Clearly, the lower symmetry of the ligand field around the V^{III} ions (C_s) is leading to greater quenching of the orbital angular momentum and removing the fitting problems caused by the latter for $[NEt_4]_3[V_2Cl_9]$. The value of J (-48 cm^{-1}) obtained is not too different from that estimated for $[NEt_4]_3[V_2Cl_9]$ by Casey and Clark,[20] and it is also similar to that for the V^{II} dinuclear complex $[V_2Cl_3(thf)_6]_2[Zn_2Cl_6]$ ($J = -37.5$ cm^{-1}) which also has a $[V_2(\mu\text{-}Cl)_3]$ core.[19]

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References

1 J. F. Branthaver, *ACS Symp. Ser.*, 1987, **344**, 188.

2 T. F. Yen, *The Role of Trace Metals in Petroleum*, Ann Arbor Science, Ann Arbor, 1975.

3 J. G. Speight, *The Desulfurisation of Heavy Oils and Residua*, Marcel Dekker, New York, 1981.

4 K. A. York, K. Folting and G. Christou, *J. Chem. Soc., Chem. Commun.*, 1993, 1563, and refs. therein.

5 N. S. Dean, K. Folting, E. Lobkovsky and G. Christou, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 594.

6 J. K. Money, J. C. Huffman and G. Christou, *J. Am. Chem. Soc.*, 1987, **109**, 2210.

7 L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 135.

8 J. R. Rambo, J. K. Money and G. Christou, manuscript in preparation.

9 J. E. Drake, J. E. Vekris and J. S. Wood, *J. Chem. Soc. A*, 1969, 345.

10 M. H. Chisholm, K. Folting, J. C. Huffman and C. C. Kirkpatrick, *Inorg. Chem.*, 1984, **23**, 1021.

11 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction, Universities of York and Louvain, 1978.

12 SigmaPlot Scientific Graphing System, Version 4.10, Jandel Corporation, 1986.

13 R. J. H. Clark, R. S. Nyholm and D. E. Scaife, *J. Chem. Soc. A*, 1966, 1296.

14 F. A. Cotton, M. W. Extine, L. R. Falvello, D. B. Lewis, G. E. Lewis, C. A. Murillo, W. Schwotzer, M. Tomas and J. M. Troup, *Inorg. Chem.*, 1986, **25**, 3505.

15 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

16 G. J. Wessel and D. J. W. Ijdo, *Acta Crystallogr.*, 1957, **10**, 466.

17 R. Bouma, J. H. Teuben, W. R. Beukema, R. L. Bansemer, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 1984, **23**, 2715.

18 F. A. Cotton and R. L. Luck, *Inorg. Chem.*, 1989, **28**, 182.

19 D. J. Bergs, M. H. Chisholm, K. Folting, J. C. Huffman and K. A. Stahl, *Inorg. Chem.*, 1988, **27**, 2950.

20 A. T. Casey and R. J. H. Clark, *Inorg. Chem.*, 1968, **7**, 1598.

21 R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, 1968, **7**, 1606.

22 B. Leuenberger and H. U. Gudel, *Mol. Phys.*, 1984, **51**, 1.

23 B. Leuenberger and H. U. Gudel, *Inorg. Chem.*, 1986, **25**, 181.

24 B. Leuenberger, B. Briat, J. C. Canit, A. Furrer, P. Fischer and H. U. Gudel, *Inorg. Chem.*, 1986, **25**, 2930.

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