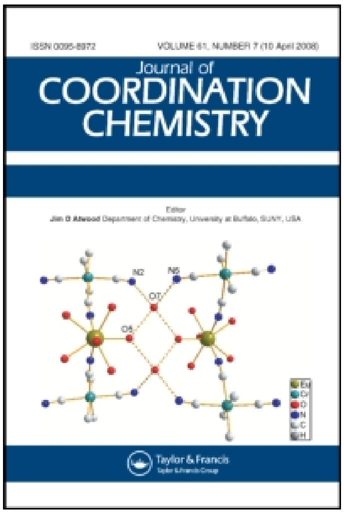

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REACTION OF EARLY TRANSITION METAL COMPLEXES WITH MACROCYCLES. IV. SYNTHESIS AND STRUCTURE OF $[(PPh_4)]_2[18\text{-CROWN-6}\cdot(VCl_4)_2]$ AND 18-CROWN-6·$VCl_3\cdot H_2O$

Ulrich Kynast[a]; Simon G. Bott[a]; Jerry L. Atwood[a]
[a] Department of Chemistry, University of Alabama, Tuscaloosa, AL, U.S.A.

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REACTION OF EARLY TRANSITION METAL COMPLEXES WITH MACROCYCLES.
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ULRICH KYNAST, SIMON G. BOTT and JERRY L. ATWOOD*

Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487, U.S.A.

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The ligand 18-crown-6 reacts with two molecules of VCl_3 in toluene to form an addition complex (**1**) in which the macrocycle functions as a terdentate ligand to each metal centre. Exposure of this compound to traces of water leads to the formation of the complex 18-crown-6·$VCl_3\cdot H_2O$ (**2**). Reaction of **1** with PPh_4Cl in dichloromethane yields $[(PPh_4)]_2[18\text{-crown-6}\cdot(VCl_4)_2]$ (**3**). Compound **2** crystallizes in the orthorhombic space group *Pbca* with $a = 16.939(9)$, $b = 12.661(9)$, $c = 17.362(9)$ Å, and $D_c = 1.57$ gcm^{-3} for $Z = 8$. Least-squares refinement based on 1549 observed reflections led to $R = 0.063$. Compound **3** crystallizes as the dichloromethane solvate in the triclinic space group $P\bar{1}$ with $a = 10.142(8)$, $b = 11.499(9)$, $c = 17.423(9)$ Å, $\alpha = 103.22(6)$, $\beta = 100.81(6)$, $\gamma = 102.84(7)°$, and $D_c = 1.49$ gcm^{-3} for $Z = 1$ with four molecules of solvent in the unit cell. $R = 0.067$ for 1874 observed reflections. In **2** two crown oxygen atoms bind directly to the metal centre at distances of 2.116(6) and 2.117(6) Å. The remaining coordination sites are occupied by three chlorine atoms and the oxygen atom of a water molecule at distances of 2.264(3)–2.303(3) and 2.018(6) Å, respectively. In **3** the macrocycle functions as a bidentate ligand to two metal centres. The V–O lengths are 2.15(1) and 2.17(1) Å, and the V–Cl, 2.301(5)–2.370(5) Å. Compound **3** also represents a rare example of a macrocycle binding to an anion, in this case, $[VCl_4]^-$.

Keywords: Vanadium, 18-crown-6, halide, structure, macrocycle

INTRODUCTION

The primary sphere coordination of crown ethers by metals other than those of Groups 1 and 2 and the f-block elements has been a sorely neglected area, despite the intense interest shown in that of the related nitrogen containing macrocycles.[1] This is rather surprising as the great flexibility and multiple binding sites of the crowns lead to these compounds having great potential for the stabilization of unusual species, especially those of the harder acid metals.[2] Recent work in our laboratory has included the investigation of some fundamental reactions, and has led to the characterization of complexes in which 18-crown-6 shows the ability to present metals with one through six oxygen atoms.[3–8] The only possible omission has been a compound in which the crown acts as a terdentate ligand, as the evidence for the existence of such a species has been ambiguous. The most reliable data obtained thus far has been the spectroscopic assignment of C_{3v} symmetry to the titanium centre in the product of the reaction of $TiCl_3$ with 18-crown-6, 18-crown-6·$(TiCl_3)_2$.[4] Unfortunately, attempts to crystallize this species were unsuccessful until water was inadvertently added to a solution to produce crystals of the complex 18-crown-6·$TiCl_3\cdot H_2O$.[4] In this contribution we report the similar behaviour of VCl_3 as well as the formation and characterization of a complex which shows that 18-crown-6 is capable of binding two metal centres.

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* Author for correspondence.

EXPERIMENTAL

All procedures were conducted using standard Schlenk techniques.

*Synthesis of 18-Crown-6·(VCl_3)$_2$ (**1**)*

(a) Vanadium trichloride (1.57 g, 10 mmol) was mixed with 18-crown-6 (1.32 g, 5 mmol) in toluene (*ca* 50 cm^3). The pink solution was concentrated and cooled to yield pink microcrystalline material in nearly quantitative yield. *Anal.*; *Calcd.* for 18-crown-6·(VCl_3)$_2$: C, 24.89; H, 4.15%. *Found*: C, 25.01; H, 4.23%.

(b) VCl_3 (1.57 g, 10 mmol) was dissolved in a melt of 18-crown-6 (5.28 g, 20 mmol). The melt was extracted with CH_2Cl_2 and the resultant pink solution was concentrated to yield the pink microcrystalline product.

*Synthesis of 18-Crown-6·VCl_3·H_2O (**2**)*

1 was dissolved in moist hexane. Concentration of the solution yielded brown crystals of **2**.

*Synthesis of [PPh_4]$_2$[18-crown-6·(VCl_4)$_2$] (**3**)*

1 (0.31 g, 0.5 mmol) was stirred with PPh_4Cl (0.37 g, 1 mmol) in CH_2Cl_2 (*ca* 25 cm^3). Concentration of the solution followed by cooling led to violet crystals of **3**.

TABLE I
Crystal data and summary of intensity data collection and structure refinement for compounds **2** and **3**.

Compound	**2**	**3**
Molecular weight	439.7	1668.3
Space group	Pbca	$P\bar{1}$
Cell constants		
a, Å	16.939 (9)	10.142 (8)
b, Å	12.66 (1)	11.499 (9)
c, Å	17.36 (1)	17.423 (9)
α, deg	90	103.22 (6)
β, deg	90	100.81 (6)
γ, deg	90	102.84 (7)
Cell vol, Å^3	3723	1867
Molecules/unit cell	8	1
D_c, gcm^{-3}	1.55	1.49
μ(calc), cm^{-1}	9.8	10.2
Radiation	Mo*Kα*	Mo*Kα*
Max crystal dimensions (mm)	0.42 × 0.68 × 1.20	0.70 × 0.60 × 0.7
Scan width, deg.	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ
Standard reflections	302,021	400,030,034
Decay of standards	< 1%	< 2%
Reflections measured	2635	3259
2 θ range, deg	2–44	2–44
Reflections considered observed ($I > 3\sigma(I)$)	1549	1874
No. of parameters varied	208	276
GOF	2.4	2.2
R	0.063	0.067
R_w	0.060	0.072

X-ray Structure Determination for **2**

Single crystals were mounted in thin-walled glass capillaries. Final lattice parameters as determined from the least-squares refinement of $(\sin\theta/\lambda)^2$ values for 24 reflections ($2\theta > 36°$) accurately centred on an Enraf–Nonius CAD-4 diffractometer are given in Table I. Data were collected by the θ-2θ scan technique as described previously.[9] A summary of data collection and structure solution parameters is also given in Table I. The intensities were corrected for Lorentz and polarization effects. Calculations were carried out using the SHELX system of computer programs.[10] Neutral atom scattering factors were taken from reference 11 and the scattering for the V and Cl atoms was corrected for the real and imaginary components of anomalous dispersion using the tabulations of Cromer and Liberman.[12]

Structure solution was accomplished initially by application of the direct methods program MULTAN,[13] which revealed the positions of the metal and its coordinated atoms. (**2** is not isostructural with its titanium analogue because of the presence of a molecule of CH_2Cl_2 of crystallization in the latter.) Difference Fourier maps phased upon these atoms afforded the coordinates of the remaining non-hydrogen atoms. At this point it was noted that the crown exhibited large thermal motion. This produced a disorder of O(6), C(10), C(11) and C(12) in a ratio 2 : 1. All atoms were treated with anisotropic thermal parameters despite the paucity of observed reflection data. All of the hydrogen atoms were geometrically positioned and allowed to ride upon the appropriate carbon atoms. Further refinement converged at reliability values of R = 0.063 and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2\}^{1/2} = 0.060$. A final difference Fourier

TABLE II
Final fractional coordinates for **2** with estimated standard deviations in parentheses.

Atom	x/a	y/b	z/c	U(eqv)*
V	0.37418(8)	0.07721(9)	0.23016(9)	.034
Cl(1)	0.4886(1)	0.1269(2)	0.1673(2)	.050
Cl(2)	0.3034(1)	0.2266(2)	0.2086(2)	.063
Cl(3)	0.3243(1)	−0.0148(2)	0.1269(2)	.057
O(1)	0.4286(3)	−0.0607(4)	0.2751(4)	.042
O(2)	0.2858(3)	0.0070(4)	0.3004(4)	.049
O(3)	0.2525(5)	0.1713(5)	0.4169(5)	.075
O(4)	0.3799(4)	0.3029(5)	0.4319(4)	.064
O(5)	0.5373(5)	0.2397(7)	0.4037(6)	.061
O(6)	0.5545(6)	0.0347(8)	0.3647(7)	.104
O(7)	0.4137(3)	0.1400(4)	0.3305(4)	.047
C(1)	0.3716(7)	−0.1391(8)	0.2971(8)	.051
C(2)	0.3085(6)	−0.0923(7)	0.3363(6)	.062
C(3)	0.2087(5)	0.0479(7)	0.3235(6)	.054
C(4)	0.2049(6)	0.0802(8)	0.4062(6)	.066
C(5)	0.2884(6)	0.1795(9)	0.4863(7)	.073
C(6)	0.3361(7)	0.2735(8)	0.4970(6)	.070
C(7)	0.4470(6)	0.3678(7)	0.4495(7)	.072
C(8)	0.5196(6)	0.3124(8)	0.4617(8)	.086
C(9)	0.6065(6)	0.181(1)	0.4221(9)	.101
C(10)	0.602(1)	0.071(2)	0.422(1)	.078
C(11)	0.5492(6)	−0.0808(8)	0.3533(7)	.069
C(12)	0.5120(5)	−0.0944(6)	0.2755(6)	.054

*U(eqv) = $1/3(U_{11} + U_{22} + U_{33})$.

showed no feature greater than 0.2 e/Å^3. The weighting scheme was based upon unit weights and no systematic variation of $w(|F_o| - |F_c|)$ *vs* $|F_o|$ or $(\sin\theta/\lambda)$ was observed. The final values of the positional parameters are given in Table II. Tables of anisotropic thermal parameters, hydrogen atom coordinates and structures are available as supplementary data from the Editor.

TABLE III

Final fractional coordinates for **3** with estimated standard deviations in parentheses.

Atom	*x/a*	*y/b*	*z/c*	*U*(eqv)*
V	0.8721(3)	1.1336(3)	0.6654(2)	.039
P	0.4683(4)	0.7169(4)	0.9029(2)	.037
Cl(1)	1.0850(4)	1.0804(4)	0.6777(3)	.046
Cl(2)	0.8099(5)	1.0178(5)	0.7512(3)	.061
Cl(3)	0.6458(5)	1.1621(5)	0.6339(3)	.064
Cl(4)	0.9677(5)	1.3244(4)	0.7657(3)	.055
Cl(5)	0.6111(7)	0.5489(6)	0.6122(4)	.109
Cl(6)	0.6993(7)	0.3872(7)	0.4913(4)	.132
Cl(7)	1.0788(8)	1.2627(7)	0.2134(5)	.140
Cl(8)	0.9225(6)	1.3219(6)	0.3324(4)	.101
O(1)	0.792(1)	0.981(1)	0.5541(6)	.042
O(2)	0.925(1)	1.2189(9)	0.5739(6)	.039
O(3)	0.814(1)	0.739(1)	0.4838(7)	.051
C(1)	0.766(2)	1.029(2)	0.4858(9)	.051
C(2)	0.892(2)	1.133(1)	0.4927(9)	.044
C(3)	1.021(2)	1.337(1)	0.581(1)	.052
C(4)	0.827(2)	0.665(1)	0.408(1)	.046
C(5)	0.681(2)	0.762(1)	0.476(1)	.046
C(6)	0.687(2)	0.866(1)	0.5456(9)	.038
C(7)	0.485(2)	0.565(1)	0.8573(9)	.039
C(8)	0.374(2)	0.459(1)	0.8329(9)	.043
C(9)	0.387(2)	0.346(2)	0.794(1)	.053
C(10)	0.515(2)	0.337(2)	0.780(1)	.068
C(11)	0.624(2)	0.438(2)	0.802(1)	.068
C(12)	0.613(2)	0.555(2)	0.844(1)	.050
C(13)	0.433(2)	0.796(1)	0.8267(9)	.040
C(14)	0.476(2)	0.769(2)	0.757(1)	.052
C(15)	0.458(2)	0.842(2)	0.703(1)	.067
C(16)	0.406(2)	0.936(2)	0.722(1)	.066
C(17)	0.356(2)	0.962(2)	0.790(1)	.071
C(18)	0.365(2)	0.893(2)	0.842(1)	.051
C(19)	0.632(2)	0.800(1)	0.9714(9)	.036
C(20)	0.704(2)	0.916(1)	0.966(1)	.044
C(21)	0.832(2)	0.980(2)	1.020(1)	.063
C(22)	0.890(2)	0.932(2)	1.078(1)	.070
C(23)	0.824(2)	0.823(2)	1.086(1)	.063
C(24)	0.693(2)	0.754(2)	1.0323(9)	.046
C(25)	0.330(2)	0.707(1)	0.9558(9)	.038
C(26)	0.194(2)	0.650(2)	0.911(1)	.061
C(27)	0.090(2)	0.639(2)	0.952(1)	.076
C(28)	0.124(2)	0.692(2)	1.035(1)	.069
C(29)	0.255(2)	0.752(2)	1.078(1)	.071
C(30)	0.366(2)	0.761(2)	1.041(1)	.055
C(31)	1.025(3)	1.228(2)	0.295(1)	.105
C(32)	0.715(3)	0.450(2)	0.595(1)	.105

*U(eqv) = $1/3(U_{11} + U_{22} + U_{33})$.

X-ray Strucutre Determination for 3

A summary of data collection parameters is given in Table I. Data collection and structure solution were carried out as for **2**. The lattice contained two crystallographically independent molecules of CH_2Cl_2 which were included in the refinement. The V, Cl, and crown atoms were treated with anisotropic thermal parameters. Refinement converged at $R = 0.067$ and $R_w = 0.072$. Final positional parameters are given in Table III, and supplementary data are available from the Editor.

RESULTS AND DISCUSSION

The spectroscopic data for **1** reveals a C_{3v} symmetry for the vanadium. Since the elemental analysis showed the complex to be of 2 : 1 stoichiometry, the most probable structure is that shown in Figure 1. Further substantiation comes from the results for compounds **2** and **3**, which possess the structures given in Figures 2 and 3, respectively. Relevant bond lengths and angles are given in Tables IV and V. Compound **2** is very similar to the analogous titanium species;[4] three chlorine atoms, an oxygen atom of a water molecule, and two crown ether oxygen atoms fill the metal coordination sphere. Further interaction occurs between the hydrogen atoms of the water molecule and macrocyclic oxygen atoms which are not bound to the metal.

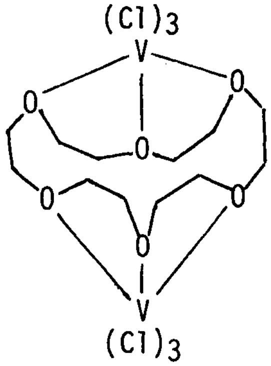

FIGURE 1 Proposed structure for 18-crown-6·$(VCl_3)_2$, **1**.

The M–O–C–C–O metallocycle in **2** is very similar to those seen previously in other bidentate complexes of 18-crown-6. Both the M–O distances (2.116(6) and 2.117(6) Å compared to 2.123(8) and 2.154(9) Å in 18-crown-6·$TiCl_3$·H_2O[4] and 2.102(4) and 2.138(4) Å in 18-crown-6·$TiCl_4$[5]) and the O–M–O angle (75.6(2)° compared to 75.5(3)° and 74.6(2)°, respectively, for the above-mentioned compounds) vary only slightly among the three adducts. This is hardly surprising in view of the slight decrease in ionic radius, 0.03 Å, seen upon moving from Ti(III) to V(III).[14] This similarity is also reflected in the average V–Cl length (2.28(1)) compared to 2.30(1) Å for the titanium analogue) and V–O(water)length (2.018(6) Å compared to 2.072(8) Å). The differences between the M–Cl lengths for the M(III) ions compared to those for the Ti(IV) complex are also in keeping with changes ionic radii.[14] Because of high thermal motion in **2**, the hydrogen atoms could not be located. However, the distances between the water oxygen atom and those of the

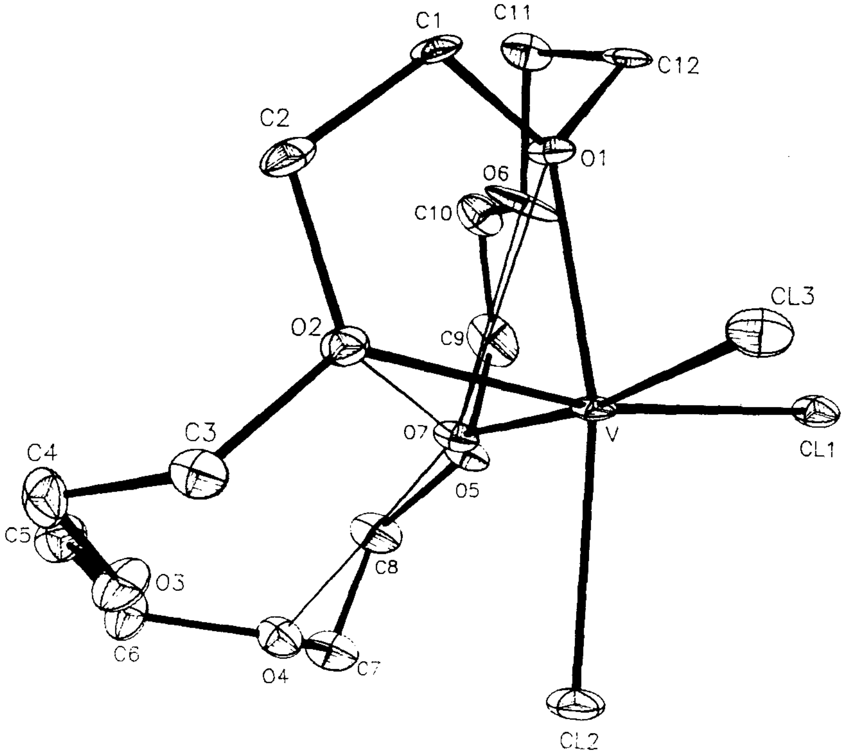

FIGURE 2 Structure for 18-crown-6·$VCl_3 \cdot H_2O$, **2**.

TABLE IV
Selected bond distances (Å) and angles (deg) for 18-crown-6·$VCl_3 \cdot H_2O$, **2**.

Atoms	Distance	Atoms	Distance
V—Cl(1)	2.303(3)	V—Cl(2)	2.264(3)
V—Cl(3)	2.289(3)	V—O(1)	2.116(6)
V—O(2)	2.117(6)	V—O(7)	2.018(6)
O(7)...O(5)	2.74	O(7)...O(4)	2.76
O(7)...O(6)	2.79	O(7)...O(3)	3.13

Atoms	Angle	Atoms	Angle
Cl(1)—V—Cl(2)	97.95(9)	Cl(1)—V—Cl(3)	94.6(1)
Cl(2)—V—Cl(3)	95.8(1)	Cl(1)—V—O(1)	91.8(2)
Cl(2)—V—O(1)	167.2(2)	Cl(3)—V—O(1)	91.6(2)
Cl(1)—V—O(2)	167.2(2)	Cl(2)—V—O(2)	94.1(2)
Cl(3)—V—O(2)	88.5(2)	O(1)—V—O(2)	75.6(2)
Cl(1)—V—O(7)	91.1(2)	Cl(2)—V—O(7)	89.3(2)
Cl(3)—V—O(7)	171.7(2)	O(1)—V—O(7)	82.3(2)
O(2)—V—O(7)	84.6(2)		

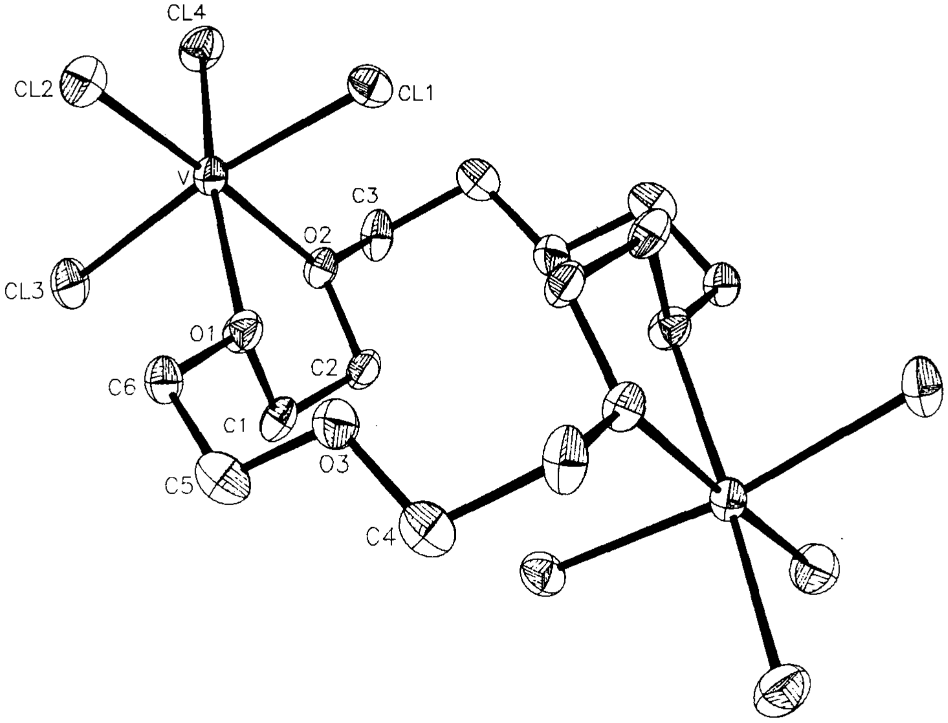

FIGURE 3 Structure of the [18-crown-6·$(VCl_4)_2]^{2-}$ anion.

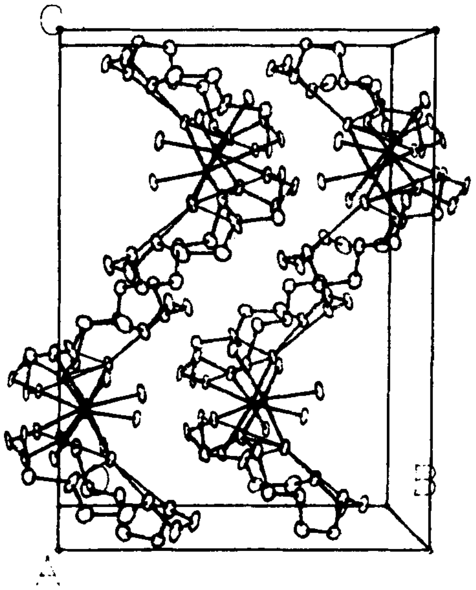

FIGURE 4 Unit cell packing for **2**, illustrating the spiral arrangement of the molecules.

crown, (O(7)...O(5) = 2.74(1), O(7)...O(4) = 2.76(1) and O(7)...O(6) = 2.79(1) Å) allow the inference of the secondary-sphere interactions observed in the titanium analogue.

The cell packing for compound **2** is shown in Figure 4, and is dominated by interactions between the chlorine atoms and crown carbon atoms. The net result of this is the formation of spiral-shaped layers in the crystal. The intra-layer chlorine ...carbon interactions are considerably stronger than the inter-layer ones, the shortest being 3.50 and 3.79 Å, respectively.

TABLE V

Selected bond distances (Å) and angles (deg) for $[18\text{-crown-6}\cdot(VCl_4)_2]^{2-}$.

Atoms	Distance	Atoms	Distance
V — Cl(1)	2.357(5)	V — Cl(2)	2.301(5)
V — Cl(3)	2.370(5)	V — Cl(4)	2.340(5)
V — O(1)	2.17(1)	V — O(2)	2.15(1)

Atoms	Angle	Atoms	Angle
Cl(1) — V — Cl(2)	89.8(2)	Cl(1) — V — Cl(3)	171.1(2)
Cl(2) — V — Cl(3)	91.5(2)	Cl(1) — V — Cl(4)	94.2(2)
Cl(2) — V — Cl(4)	96.5(2)	Cl(3) — V — Cl(4)	94.3(2)
Cl(1) — V — O(1)	87.0(3)	Cl(2) — V — O(1)	96.1(3)
Cl(3) — V — O(1)	84.2(3)	Cl(4) — V — O(1)	167.3(3)
Cl(1) — V — O(2)	87.9(3)	Cl(2) — V — O(2)	172.6(3)
Cl(3) — V — O(2)	89.7(3)	Cl(4) — V — O(2)	90.7(3)
O(1) — V — O(2)	76.7(4)	V — O(1) — C(1)	109.7(9)
V — O(1) — C(6)	123.7(8)	C(1) — O(1) — C(6)	113(1)
V — O(2) — C(2)	114.4(8)	V — O(2) — C(3)	130.9(9)

The existence of the crown complex in the form of a 2- anion in **2** leads to longer bond lengths, each of the metal-ligand bonds increasing by about 0.05 Å ($V–O_{av}$ = 2.16(1) Å, $V–Cl_{av}$ 2.32(2) Å trans to O). This sensitivity of the crown oxygen–metal bonds to the environment is unusual, and perhaps reflects the stability of the crown conformation in which only two oxygen atoms point towards the centre of the macrocycle. In the absence of a complexed cation, crown ethers tend to achieve a balance between torsional strain and that induced by oxygen... oxygen repulsions. Compound **2** and its structural analogues, contain the crown in a highly unstable conformation, as evidenced by the manner in which the crown uses its uncomplexed portion to relax the torsional strain induced by the metallic species (Table VI). This leads to close O... O interactions. The macrocycle in compound **3** has no means of relaxing sufficiently so that the ideal torsional situation can be achieved, and therefore compromises by increasing the distance between the oxygen atoms. Thus, the coordination is weaker to the vanadium as less electron density must be removed from the oxygen atoms.

It should be noted in passing that crown ether complexes bearing an overall negative charge are rather rare. The only previously reported example is $[18\text{-Crown-6}\cdot Na(P(CN)_2)_2]^-$,[15] an anion which derives its charge from the coordination of the two phosphide anions by the sodium cation. Although anionic complexes would obviously have greatly increased cation-binding properties, that of compound **3** has no remaining cavity due to the unusual configuration of the crown, and data on cation binding cannot be obtained.

Complex **3** crystallizes with four molecules of dichloromethane, which are arranged in the middle of a cavity defined by two ion pairs, as shown in Figure 5. This cavity is formed through interactions between the aromatic rings of the cation and the chlorine atoms trans to the oxygen atoms of the anion, allowing the solvent molecules to fit inside at normal van der Waals contacts.

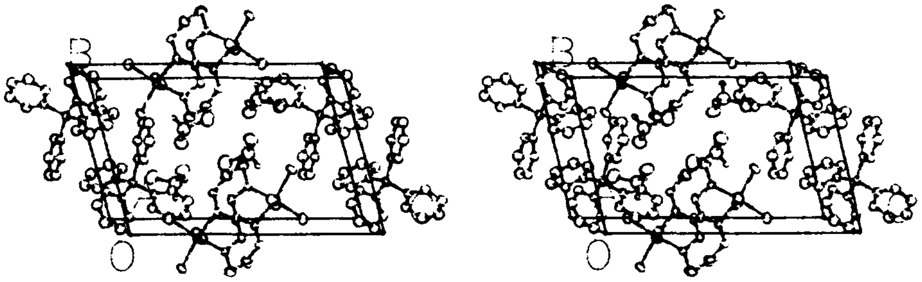

FIGURE 5 Stereoscopic view of the cell packing for **3**.

ACKNOWLEDGEMENT

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