

Preparation and structure of $[(\eta\text{-C}_5\text{H}_5)_2\text{VCl}][(\eta\text{-C}_5\text{H}_5)\text{VCl}_2](\mu\text{-O})$, a paramagnetic organometallic complex with an asymmetric oxo bridge

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Abstract

The reaction between Ag_2O or Ag_2CO_3 and an equimolar mixture of Cp_2VCl_2 and CpVCl_3 ($\text{Cp} = \eta\text{-C}_5\text{H}_5$) gave $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$. The product consists of $[\text{Cp}_2\text{VCl}]$ and $[\text{CpVCl}_2]$ units linearly bridged by oxygen, with a $\text{Cp}_2\text{VCl-O}$ distance of 1.993(5) Å and a $\text{CpVCl}_2\text{-O}$ distance of 1.653(5) Å. The difference in V-O distances and the paramagnetism of the complex are ascribed mainly to V-O π -bonding. Crystal data: orthorhombic, *Pnma*, *a* 10.321(1) *b* 12.774(1) *c* 12.711(1) Å, *Z* = 4; Mo- K_α -radiation, *R* = 0.043 for 954 observed reflections and 127 parameters.

Introduction

Organovanadium complexes containing bridging oxygen atoms are relatively rare. Apart from clusters containing μ_3 - and sometimes μ_2 -oxygen atoms [1–3], the only complexes containing μ_2 -oxygen are $[\text{CpVI}]_2[\text{CpV}(\text{NO})]_2(\mu\text{-O})_4$ ($\text{Cp} = (\eta\text{-C}_5\text{H}_5)$), $[\text{Cp}^*\text{VCl}(\mu\text{-O})]_4$, $[\text{Cp}^*\text{VI}_2]_2(\mu\text{-O})$ and $[\text{Cp}^*\text{VI}(\text{O})]_2(\mu\text{-O})$ ($\text{Cp}^* = \eta\text{-C}_5(\text{CH}_3)_5$) [4,5]. An asymmetric dimer $[\text{Cp}_2\text{VCl}][\text{CpVCl}](\mu\text{-O})_2$ has been proposed but not adequately characterised [6]. In contrast to vanadium there are a large number of μ_2 -oxo bridged complexes of cyclopentadienyltitanium [7,8] and also of molybdenum [9]. There are no asymmetrical dimers, though the trimer $[\text{Cp}_2\text{TiCl}]_2[(\mu\text{-O})_2\text{TiCp}]$ [10] can be considered as two such dimers linked together. We have therefore attempted to obtain asymmetrical dimers of vanadium, and report here on the preparation and structure of $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$.

Experimental

All operations were conducted under argon or vacuum using standard vacuum line and Schlenk tube techniques. Solvents were pre-dried, stored under vacuum

over methyllithium and the starting materials CpVCl_3 [11] and Cp_2VCl_2 [12] were prepared by the methods cited. Ag_2CO_3 was freshly prepared from AgNO_3 and Na_2CO_3 according to ref. [13]; other chemicals were reagent grade. Instruments used were a Perkin-Elmer 683 infrared spectrophotometer, a Varian XL-200 NMR spectrometer and an Enraf-Nonius CAD4 diffractometer. Microanalyses were by Beller Laboratorium, Göttingen, FRG, mass spectra by the Mass Spectrometer Facility at the University of Alberta.

μ -Oxo[chlorobis(cyclopentadienyl)vanadium][dichloro(cyclopentadienyl)vanadium]

To an equimolar solution of CpVCl_3 (0.13 g, 0.58 mM) and Cp_2VCl_2 (0.13 g, 0.52 mM) in tetrahydrofuran (50 cm³) was added freshly prepared Ag_2CO_3 (0.31 g, 1.12 mM). The dark purple solution became light green and a greenish white precipitate formed. After 24 h the tetrahydrofuran was removed under vacuum and the residue was extracted twice with CH_2Cl_2 , giving a lime-green solution (50 cm³). Addition of ether (25 cm³) precipitated green $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$ (0.058 g, 27%). On setting a solution of the complex in CH_2Cl_2 /ether aside for several weeks, crystals of $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$ suitable for an X-ray diffraction study were formed. Anal. Found: C, 44.1; H, 4.1; Cl, 24.1; V, 24.3. $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{OV}_2$ calcd.: C, 42.9; H, 3.6; Cl, 25.3; V, 24.3%. Judging by the analyses there was ether in the crystals, but this could not be confirmed by the crystallographic study. Infrared: 880 cm⁻¹ (m), $\nu(\text{V-O})$. NMR, ¹H (CDCl_3 solution): 8.7 ppm (very broad). Mass spectrum. m/e 216 ($[\text{Cp}_2\text{V}^{35}\text{Cl}]^+$); 186 ($[\text{CpVCl}_2]^+$); 181 ($[\text{Cp}_2\text{V}]^+$); 151 ($[\text{CpVCl}]^+$).

Determination of the crystal and molecular structure of $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$

Crystals obtained as described above were coated with Apiezon grease, mounted in sealed tubes and examined by photographic and diffractometric methods. Crystal data: $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{OV}_2$, $M = 419.53$; orthorhombic $Pnma$, a 10.321(1) b 12.774(1) c 12.711(1) Å; $Z = 4$; D_c 1.66 Mg m⁻³; crystal dimensions 0.27 × 0.27 × 0.31 mm; Mo- K_α -radiation, λ 0.71073 Å; μ 1.56 mm⁻¹. The intensities of 1530 unique reflections ($2\theta < 50^\circ$) were measured by the ω - 2θ scan method at room temperature; 954 reflections were judged as observed ($I \geq 2.5\sigma(I)$) and these were used for the structure determination. No absorption correction was applied. The final R [$= \sum \Delta |F| / \sum |F_o|$] was 0.043, R_w [$= (\sum w(\Delta F)^2 / \sum w F_o^2)^{1/2}$] 0.047 and the goodness of fit [$= (\sum w(\Delta F)^2 / (\text{No. of reflections} - \text{no. of parameters}))$] was 1.30. The number of variables was 127, including an extinction coefficient. The maximum residual intensity in the final difference map was 0.35 e Å⁻³ and the minimum was -0.40 e Å⁻³.

Preliminary positions for the vanadium atoms were found using the MULTAN-80 program [14]. The positions of these atoms were used in the phasing of a Fourier synthesis and the positions of all non-hydrogen atoms were determined by successive Fourier, difference Fourier and partial refinement techniques. The structure was refined by a standard least-squares technique, minimizing the function $\sum w(\Delta F)^2$ with a weighting scheme of the form $w = 1/(\sigma((F)^2 + kF^2))$ based on counting statistics. Scattering factors were taken from International Tables for X-ray Crystallography [15] and were corrected for both the real and imaginary parts of the anomalous dispersion where appropriate. Final refinement was with anisotropic thermal parameters for all atoms except hydrogen. The hydrogen atom positions were refined, the thermal parameter being fixed. The diffractometer was operated

Table 1

Atomic positions for the non-hydrogen atoms of $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$.

	x	y	z
V(1) ^a	0.02638(13) ^b	0.75	0.58360(9)
V(2)	0.33005(12)	0.75	0.43724(8)
Cl(1)	0.05785(19)	0.88395(19)	0.70044(15)
Cl(2)	0.2025(3)	0.75	0.28253(15)
O(1)	0.1642(5)	0.75	0.5174(3)
C(11)	-0.0870(10)	0.75	0.4334(9)
C(12)	-0.1249(8)	0.6640(7)	0.4878(7)
C(13)	-0.1882(6)	0.6978(5)	0.5789(6)
C(21)	0.3066(12)	0.9246(6)	0.4275(11)
C(22)	0.4028(19)	0.8982(9)	0.3598(9)
C(23)	0.4935(12)	0.8646(10)	0.4178(13)
C(24)	0.4601(11)	0.8663(7)	0.5250(9)
C(25)	0.3408(8)	0.9054(5)	0.5276(7)

^a For numbering scheme see Fig. 1. ^b Estimated standard deviations are given in brackets.

Table 2

Important distances (Å) and angles (°) in $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$

V(1)–O ^a	1.652(5) ^b	V(2)–O	1.993(5)
V(1)–Cl(1)	2.289(2)	V(2)–Cl(2)	2.367(2)
V(1)–C(11)	2.239(10)	V(2)–C(21)	2.247(7)
V(1)–C(12)	2.264(7)	V(2)–C(22)	2.262(10)
V(1)–C(13)	2.314(6)	V(2)–C(23)	2.247(10)
V(1)–Cp ^c	1.958(10)	V(2)–C(24)	2.292(9)
V(1)–O–V(2)	179.8(3)	V(2)–C(25)	2.296(6)
Cl(1)–V(1)–Cl(1')	96.75(10)	V(2)–C(aver)	2.269(8)
O–V(1)–Cl(1)	102.0(1)	V(2)–Cp ^c	1.961(7)
		O–V(2)–Cl(2)	86.9(1)
		Cp–V(2)–Cp'	135.1

^a For the numbering scheme see Fig. 1. There is a plane of symmetry containing C(11), V(1), O, V(2) and Cl(2). ^b Estimated standard deviations are given in brackets. ^c Cp is the plane of the C₅ ring.

Table 3

Planes of the cyclopentadienyl rings in $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$ ^a

Plane 1. C(11), C(12), C(13) ^b (Cp(1))			
8.99(3)X + 0.00(17)Y + 6.25(7)Z = 1.93(14)			
V(1) 1.958(10)			
Plane 2. C(21), C(22), C(23), C(24), C(25) (Cp(2))			
3.87(7)X + 11.81(4)Y + 0.95(10)Z = 12.51(4)			
C(21)	0.000(17)	C(24)	-0.002(15)
C(22)	-0.004(23)	C(25)	0.001(12)
C(23)	0.004(21)	V(2)	-1.961(7)

^a All equations and distances are in Å. ^b For numbering scheme see Fig. 1.

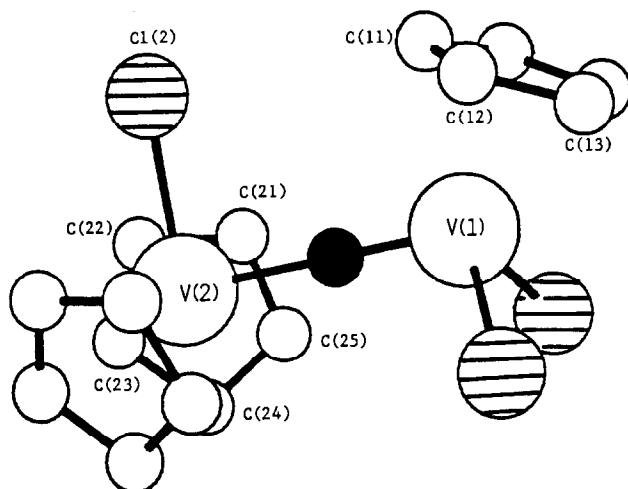


Fig. 1. Molecular Structure and Numbering Scheme for $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$.

under the control of the NRCCAD software [16] and the refinement used the NRCVAX system of programs [17].

The positional parameters for the non-hydrogen atoms of $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$ are given in Table 1, important bond distances and angles are given in Table 2, and equations for planes in the cyclopentadienyl rings in Table 3. The numbering scheme is shown in Fig. 1. Tables of hydrogen atom positions, thermal parameters, equations of some mean planes, comprehensive lists of bond distances and angles and a table of $|F_o|$ and $|F_c|$ are available as supplementary material*.

Results and discussion

The dimer $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$ was readily obtained by reaction of an equimolar mixture of Cp_2VCl_2 and CpVCl_3 with either Ag_2O (eq. 1) or Ag_2CO_3 (eq. 2).



Surprisingly there was no reaction between Ag_2O or Ag_2CO_3 and either Cp_2VCl_2 or CpVCl_3 alone. Neither was there any reaction between Cp^*VCl_3 and Ag_2CO_3 ; from $\text{Cp}_2^*\text{VCl}_2$ and Ag_2CO_3 only an intractable polymer was obtained. An intermolecular redox process may be responsible for the loss of Cl^- required for formation of the oxo bridge.

The dimer consists of a Cp_2VCl unit and a CpVCl_2 unit bridged by an oxygen atom. Both vanadium atoms are formally V^{IV} , d^1 , and the dimer is paramagnetic. The $\text{V}-\text{O}-\text{V}$ angle is $179.8(3)^\circ$ and the two halves of the molecule are arranged so that the Cp ring of the CpVCl_2 unit eclipses the Cl ligand of the Cp_2VCl unit. The primary reason for this arrangement is presumed to be steric since it minimises the interaction between the Cp rings. The molecule possesses a crystallographic plane of

* Copies may be purchased from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0S2.

symmetry which passes through both vanadium atoms, Cl(2), the oxygen atom, and C(11) of the unique Cp ring (see Fig. 1). The $\text{Cp}_2\text{VCl}(\mu\text{-O})$ unit is formally eight-coordinate and has the standard pseudo-tetrahedral arrangement of ligands around vanadium. The $\text{CpVCl}_2(\mu\text{-O})$ unit is a six-coordinate piano stool. The difference in coordination number is clearly reflected in the V–Cl distances. These measure 2.367(2) Å in the Cp_2VCl unit, compared to 2.398(2) Å in $(\text{C}_5\text{H}_4\text{CH}_3)_2\text{VCl}_2$ [18], and 2.289(1) Å in the CpVCl_2 unit, compared to 2.294(5) Å in $[\text{Cp}^*\text{VCl}(\mu\text{-O})]_4$ [5].

The most remarkable facet of the V–O–V bridge is the very large difference (0.341 Å) in the V–O distances; that to the Cp_2VCl unit is 1.993(5) Å, that to the CpVCl_2 unit, 1.652(5) Å. Some of this difference is undoubtedly due to the different coordination numbers around the vanadium atoms. However the difference in the V–Cl distances (0.078 Å), which can only be ascribed to the different coordination numbers, represents only 3% of the V–Cl distance whereas the difference in the V–O distances represents 19%. We therefore believe that V–O π -bonding is the major reason for the difference in the V–O distances. This conclusion is supported by an examination of the Ti–Cl and Ti–O distances in $[\text{Cp}_2\text{TiCl}]_2[(\mu\text{-O})_2\text{TiCp}]$ [10]. In this compound the Ti–Cl distances in the eight-coordinate $\text{Cp}_2\text{TiCl}(\mu\text{-O})$ fragment average 2.385(4) Å, that in the six-coordinate $\text{CpTiCl}(\mu\text{-O})_2$ unit 2.330(3) Å. The difference, 0.055 Å, is due to the difference in the coordination numbers, and is comparable to that found in $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$ (0.078 Å). The difference between the average Cp_2TiCl –O and CpTiCl –O distances, on the other hand, is only 0.109 Å, considerably smaller than observed in $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$ (0.341 Å).

Both V atoms are formally V^{IV} , d^1 . In the $\text{Cp}_2\text{VCl}(\mu\text{-O})$ unit six metal orbitals are used for bonding to Cp, leaving the three orbitals described by Lauher and Hoffmann for a Cp_2MX_2 molecule to accommodate the V–Cl and V–O σ -bonds and the single d electron [19]. This single electron will be in the $1a^1$ orbital (in the C_{2v} symmetry of Cp_2MX_2). There can be π -bonding to this orbital from the filled π -orbitals of both Cl and O [20] but such an interaction will push $1a^1$ to higher energy and so partially cancel the π -bond formed. The $\text{CpVCl}_2(\mu\text{-O})$ unit has piano-stool geometry and the single d electron resides in one of the three orbitals which are the remnants of the t_{2g} set found in an octahedral ML_6 molecule. Two of these orbitals are empty and available for π -bonding to the oxygen and chlorine ligands. A short CpVCl_2 –O distance is therefore expected. In $[\text{Cp}_2\text{TiCl}]_2[(\mu\text{-O})_2\text{TiCp}]$ [10], which contains Ti^{IV} , the π interaction between Cl or O and Cp_2Ti is not cancelled since there are no d electrons on the titanium atoms. The result is more symmetrical Ti–O distances.

The π -bonding to the CpVCl_2 unit is reflected in the physical properties of the compound. The CpVCl_2 –O distance (1.652(5) Å) approaches the 1.60 Å value generally found for the $\text{V}^{\text{IV}}=\text{O}$ moiety in six coordinate compounds. The V–O single bond distance in such compounds is closer to 2.05 Å [21]. The $\nu(\text{V}-\text{O})$ frequency of 880 cm^{-1} is extremely high, approaching the $\nu(\text{V}=\text{O})$ frequency of 965 cm^{-1} found in $\text{Cp}^*\text{VCl}_2(\text{O})$ [5]. The V–O π -bonding is large enough for the oxygen atom to exert a significant *trans*-affect on the C_5H_5 ring. The V–C distance to C(13) (*trans* to O) is 2.314(6) Å, to C(12), 2.264(7) and to C(11), 2.239(10) Å. The *trans*-affect of the doubly-bonded oxygen ligand has been noted in $\text{Cp}^*\text{ReL}_2(\text{O})$ compounds previously [22,23]; it also occurs in $\text{Cp}^*\text{VCl}_2(\text{O})$ [5].

The steric requirements of the Cp ring which dictate the configuration of the two halves of the dimer about the V–O–V axis, together with the π -bonding, explain the paramagnetism of $[\text{Cp}_2\text{VCl}][\text{CpVCl}_2](\mu\text{-O})$. The two orbitals on the CpVCl_2 unit which are involved in the π -bonding to oxygen are mutually orthogonal and will lie in the xz and yz planes if the V–O–V axis is defined as z . The third orbital holding the single d electron will then lie in the xy plane, perpendicular to z . Because of the steric requirements the Cp_2VCl unit is aligned about z so that the Cl and O ligands, and the $1a^1$ orbital on this unit which carries the single electron, lie in the yz plane of the molecule. Consequently, the two electrons, one on each vanadium, must remain unpaired.

We are attempting to prepare other unsymmetrical oxo-bridged dimers with varying numbers of d electrons on each metal. Such molecules should provide a good test of bonding theories for this type of molecule.

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