



## Note

# Bis(aqua)bis( $\eta^5$ -cyclopentadienyl)vanadium(IV) bis(trifluoromethanesulfonate) tetrahydrofuran solvate: Synthesis and characterization

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## ABSTRACT

The reactivity pattern of  $[\text{V}(\text{Cp})_2\text{Cl}_2]$  towards the weakly coordinating  $\text{CF}_3\text{SO}_3^-$  anion in the absence of chelating or bridging organic ligands has been investigated, where  $\text{Cp}^-$  is the  $\eta^5\text{-C}_5\text{H}_5^-$  ligand. The synthesis, single-crystal X-ray structure and physical/spectroscopic characterization are reported for the product  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2\cdot\text{THF}$  (**1**·THF). The coordination about the  $\text{V}^{\text{IV}}$  atom, formed by the two  $\text{H}_2\text{O}$  molecules and the centroids of the cyclopentadienyl rings, is distorted tetrahedral. The  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]^{2+}$  cation is connected to the triflate anions via hydrogen bonds. Magnetic susceptibility, EPR and IR data are discussed in terms of the nature of bonding and the structure of the complex.

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## 1. Introduction

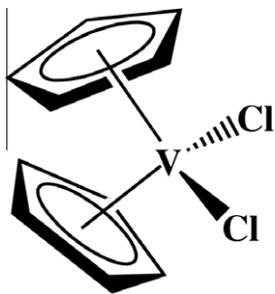
The first organometallic compounds of vanadium with a V-to-ligand  $\pi$  or  $\sigma$  bond were characterized in 1953,  $[\text{V}(\text{Cp})_2\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ), and 1960,  $[\text{V}(\text{Ph})\text{Cl}_3]$ , respectively [1], where  $\text{Cp}^-$  is the cyclopentadienyl(−1) ligand ( $\text{C}_5\text{H}_5^-$ ) and  $\text{Ph}^-$  is the phenyl group. Progress in this area had been relatively slow until the 1980s. During the last two decades, organovanadium chemistry has experienced an explosive development and compounds covering the oxidation states −III, e.g. in  $[\text{V}(\text{CO})_5]^{3-}$ , to +V, e.g. in  $[\text{VO}(\text{Cp}^*)(\text{Me})_2]$ , where  $\text{Cp}^{*-}$  is the pentamethylcyclopentadienyl(−1) ligand [1], have been prepared.

An important class of organometallic V compounds consists of those containing one (half-sandwich complexes) or two (sandwich and bent sandwich complexes)  $\text{Cp}^-$  groups or their analogs. The ligands are usually coordinated in the  $\eta^5$  mode. Cp complexes exist with the V center in oxidation numbers −I to +V, e.g. compounds  $[\text{V}^{\text{I}}(\text{Cp})(\text{CO})_3]^-$ ,  $[\text{V}^{\text{0}}(\text{Cp})(\text{Tp})]$  ( $\text{Tp}^+$  is the propylm cation,  $\eta^7\text{-C}_7\text{H}_7^+$ ),  $[\text{V}^{\text{I}}(\text{Cp})(\text{CO})_4]$ ,  $[\text{V}^{\text{II}}(\text{Cp})_2]$ ,  $[\text{V}^{\text{III}}(\text{Cp})_2\text{Cl}]$ ,  $[\text{V}^{\text{IV}}(\text{Cp})_2(\text{Me})_2]$  and  $[\text{V}^{\text{VO}}(\text{Cp}^*)(\text{Ph})_2]$ , demonstrating the versatility of valence electronic configurations suitable for binding to this ligand. The most com-

mon oxidation state of the metal with  $\text{Cp}^-$  ligation is the +IV, examples being the vanadocene dihalide and bis(pseudoalide) complexes,  $[\text{V}(\text{Cp})_2\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{N}_3, \text{NCS}, \text{NCO}, \dots$ ) [2,3]. Interest in V/Cp<sup>−</sup> compounds with respect to potential applications arises from their use as catalysts, employment in organic synthesis, anti-tumor properties and their importance in bioinorganic chemistry. Examples of catalytic processes using such species are the  $[\text{V}(\text{Cp})_2\text{Cl}_2]/\text{Al}(\text{Et})_2\text{Cl}$  systems in the Ziegler–Natta polymerization of ethylene [4]. The importance of V/Cp<sup>−</sup> complexes in organic synthesis has been demonstrated by the use of  $[\text{V}(\text{Cp})(\text{H})(\text{CO})_3]^-$  in the preparation of alkanes from alkyl bromides and of aldehydes from carbonic acid chlorides [5]. Complexes of the  $\{\text{V}^{\text{IV}}(\text{Cp})_2\}^{2+}$  moiety exhibit antitumor and antiproliferative properties, both *in vitro* and *in vivo*, primarily via oxidative damage [6]. A comparison test in the human testicular cancer cell lines Tera-2 and Ntera-2, using both 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide assays and apoptosis assays, led to the conclusion that the  $[\text{V}(\text{Cp})_2(\text{NCS})_2]$  was most potent [7]. Very recently, *in vitro* experiments of dichloridobis[(*p*-methoxybenzyl)( $\eta^5$ -cyclopentadienyl)]vanadium(IV) and its diselenocyanate-derivative on the CAKI-1 cell line showed impressive cytotoxic effects with IC50 values in the nanomolar range, for the first time for metallocene anticancer drug candidates [8a]. Further biological studies in structurally similar compounds have also revealed the potential of this family of

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**Scheme 1.** The starting material dichloridobis( $\eta^5$ -cyclopentadienyl)vanadium(IV) or vanadocene dichloride,  $[V(Cp)_2Cl_2]$ .

compounds in the treatment of various cancer cell lines [8b–d]. Compound  $[V(Cp)_2(acac)](CF_3SO_3)$  is a dual-function anticancer agent with anti-angiogenic and anti-mitotic properties against human cancer cells [9]. Finally, the crystal structure of the product of the reaction between aqueous  $[V(Cp)_2Cl_2]$  and diphenyl phosphate, namely  $[V(Cp)_2(H_2O)_2](O_2P(OPh)_2)_2$  [10], shows that the interaction of  $V^{IV}$  with phosphate is an outer-sphere process; this structure offers a model for the interaction of the antitumor unit  $\{V(Cp)_2\}^{2+}$  with DNA in that diesterified phosphoric acids exhibit metrical parameters about the phosphate similar to those in DNA [10].

We have a long-standing interest in the reactivity chemistry of  $Cp^-$ ,  $Cp^{*-}$  or other substituted derivatives of  $Ti^{IV}$ ,  $Zr^{IV}$ ,  $Hf^{IV}$  and  $V^{IV}$  (metallocenes) with either organic or inorganic ligands which results in structurally interesting products [2,11–14]. For example, we have reported that the reaction of  $[Ti(Cp)_2Cl_2]$  and 2,6-bis(3,5-dimethylpyrazolyl-1-yl)pyridine (bdmpp) in acetone proceeds with the complete substitution of the cyclopentadienyl ligands and affords complex  $[Ti^{IV}Cl_2(O_2)(bdmpp)]$  containing the side-on ( $\eta^2$ )  $O_2^{2-}$  group [11]. Also we have recently discovered that the reaction of  $[Ti(Cp)_2I_2]$  with MeOH and  $H_2O$  surprisingly leads to the trinuclear complex  $[Ti^{IV}_3O(OMe)_6(Cp)_3(I_3)]$  possessing a triangular, oxide-centered topology [14]. As part of a broad research program to investigate the reactivity of  $[M(Cp)_2X_2]$  compounds ( $M = Ti, Zr, Hf, V$ ;  $X = \text{halide or pseudohalide}$ ), this report describes the reaction of vanadocene dichloride (Scheme 1) with the weakly coordinating anion (WCA)  $CF_3SO_3^-$  in the absence of ancillary chelating or bridging organic ligands and the full characterization of the product  $[V(Cp)_2(H_2O)_2](CF_3SO_3)_2$ . Reactions of metallocene complexes with WCAs are of current interest because their products are important in catalysis [15]. For example, complexes of the type  $[M(Cp')_2(Me)(WCA)]$  ( $M = Ti, Zr, Hf$ ;  $Cp'^- =$  substituted cyclopentadienyl) are utilized as catalysts for the polymerization of alkenes  $CH_2=CHR$  ( $R = H, \text{alkyl, aryl}$ ) [16]. It is universally accepted that polymerization involves initial substitution of the WCA by the alkene to generate a cationic alkene intermediate,  $[M(Cp')_2(Me)(\eta^2-CH_2=CHR)]^+$ , and that the latter then undergoes migratory insertion to give an alkyl intermediate,  $[M(Cp')_2(\eta^1-CH_2CHMeR)]^+$ , with subsequent steps involving a series of similar insertion reactions.

## 2. Experimental

### 2.1. General and physical measurements

Most manipulations were performed under aerobic conditions using materials and solvents (Merck, Alfa Aesar) as received.  $[V(Cp)_2Cl_2]$  was synthesized by the 1:2:2 reaction of  $VCl_4$ , CpH and  $Bu^tLi$  in THF/petroleum ether under inert conditions (Ar atmosphere) according to a published procedure [2].

Elemental analyses (C, H, S) were conducted at the in-house Microanalytical Service using an EA 1108 Carlo Erba analyser. IR spectra ( $4000\text{--}500\text{ cm}^{-1}$ ) were recorded on a Perkin Elmer 16PC FT spectrometer with samples prepared as KBr pellets. The magnetic susceptibility of the product was measured at  $20^\circ\text{C}$  by the Faraday method with a Cahn–Ventron RM-2 balance standardized with  $[HgCo(SCN)_4]$ . The molar susceptibility was corrected  $[(\chi_M)_{\text{corr}}]$  for the diamagnetism of the constituent atoms using Pascal's constants. The effective magnetic moment,  $\mu_{\text{eff}}$ , was calculated from the equation  $\mu_{\text{eff}} = 2.83[(\chi_M)_{\text{corr}}T]^{1/2}$ . The EPR spectrum in DMSO solution was recorded on a Bruker ES200 X-band spectrometer at room temperature ( $25^\circ\text{C}$ ).

### 2.2. Synthesis of $[V(Cp)_2(H_2O)_2](CF_3SO_3)_2 \cdot THF$ (**1**·THF)

A colourless solution of  $Ag(CF_3SO_3)$  (0.257 g, 1.0 mmol) in THF (5 mL) was added to a green suspension of  $[V(Cp)_2Cl_2]$  (0.126 g, 0.5 mmol) in the same solvent (5 mL) under vigorous stirring. A white precipitate of AgCl formed immediately and the colour of the reaction mixture turned to deep green. After stirring for 10 min, AgCl was removed by filtration and the deep green filtrate was stored for 24 h at room temperature in a covered tube filled with Ar gas. X-ray quality green–brown, plate-like crystals of the product were deposited on the walls of the tube. The crystals were collected by filtration, washed with  $Et_2O$  ( $2 \times 3\text{ mL}$ ), dried in air for 15 min and kept under Ar (the product slowly decomposes in air). Yield: 0.105 g (36%). Anal. Calc. for  $C_{16}H_{22}F_6O_9S_2V$ : C, 31.71; H, 3.78; S, 10.92. Found: C, 31.92; H, 3.71; S, 11.07%. M.p.  $104^\circ\text{C}$ . IR data (KBr pellet,  $\text{cm}^{-1}$ ):  $\nu = 3280, 3094, 1444, 1256, 1178, 1034, 880, 822, 766, 646, 578, 520\text{ cm}^{-1}$ . Effective magnetic moment ( $20^\circ\text{C}$ ):  $\mu_{\text{eff}} = 1.74\text{ B.M.}$  EPR (DMSO):  $g = 1.981(2)$ ,  $\langle A \rangle = 67.8 \times 10^{-4}\text{ cm}^{-1}$ .

### 2.3. Single-crystal X-ray crystallography

A green–brown, plate-like crystal of **1** THF ( $0.10 \times 0.39 \times 0.49\text{ mm}$ ) was taken from the mother liquor and immediately

**Table 1**  
Crystallographic data for complex **1**·THF.

Formula	$C_{16}H_{22}F_6O_9S_2V$
$M_r$	587.40
Crystal size (mm)	$0.10 \times 0.39 \times 0.49$
Colour, habit	green–brown, plates
Crystal system	monoclinic
Space group	$P2_1/n$
$a$ (Å)	8.1577(1)
$b$ (Å)	21.0261(3)
$c$ (Å)	13.4999(2)
$\beta$ ( $^\circ$ )	90.936(2)
$V$ (Å <sup>3</sup> )	2315.26(6)
$Z$	4
$D_{\text{calcd}}$ ( $\text{g cm}^{-3}$ )	1.685
$\mu$ (Cu $K\alpha$ ), ( $\text{mm}^{-1}$ )	6.153
$F(000)$	1196
$T$ (K)	160(2)
$\theta$ range ( $^\circ$ )	6.64–65.00
Ranges	
$h$	$-9 \rightarrow 9$
$k$	$-17 \rightarrow 24$
$l$	$-15 \rightarrow 12$
Measured reflections	16123
Unique reflections ( $R_{\text{int}}$ )	3803 (0.0555)
Reflections used [ $I > 2\sigma(I)$ ]	3402
Goodness-of-fit (GoF) on $F^2$	1.075
$R_1^a$ [ $I > 2\sigma(I)$ ]	0.0396
$wR_2^b$ [ $I > 2\sigma(I)$ ]	0.1016
$(\Delta\rho)_{\text{max}}/(\Delta\rho)_{\text{min}}$ ( $e \text{ \AA}^{-3}$ )	0.339/–0.535

<sup>a</sup>  $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$ .

<sup>b</sup>  $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ .

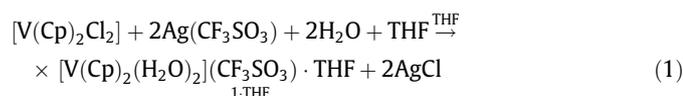
cooled to  $-113\text{ }^{\circ}\text{C}$ . Diffraction data were collected on a Rigaku R-AXIS SPIDER Image Plate diffractometer equipped with a graphite monochromator utilizing Cu  $K\alpha$  radiation. Data collection ( $\omega$  scans) and processing (cell refinement, data reduction and empirical absorption correction) were performed using the CRYSTALCLEAR program package [17]. Important crystal data and parameters for data collection and refinement are listed in Table 1.

The structure was solved by direct methods using SHELXS-97 [18] and refined by full-matrix least-squares techniques on  $F^2$  with SHELXS-97 [19]. The H atoms of the disordered molecules (see below) were introduced at calculated positions as riding on bonded atoms. All the rest H atoms were located by difference maps and refined isotropically. All non-H atoms were refined anisotropically. The C atoms of one of the two  $\text{Cp}^-$  rings [C(6)–C(10)] as well as the C atoms of the lattice THF molecule were found disordered over two orientations and refined with occupation factors summing one.

### 3. Results and discussion

#### 3.1. Brief synthetic comments and characterization studies

The 1:2 reaction between  $[\text{V}(\text{Cp})_2\text{Cl}_2]$  and  $\text{Ag}(\text{CF}_3\text{SO}_3)$  in THF is accompanied by a colour change from green to deep green–brown and quantitative precipitation of  $\text{AgCl}$ . Removal of the white precipitate by filtration and storage of the filtrate at room temperature gives crystals of  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{THF}$  (**1**·THF) in moderate yield. The aqua ligands most probably originate from the moisture of the solvent which was not distilled. The preparation of the product is summarized in the balanced Eq. (1).



The bulk magnetic susceptibility measurement on **1**·THF gave a value of  $\mu_{\text{eff}} = 1.74$  B.M., which is very close to the spin-only value for one unpaired electron ( $3d^1$  system) [3]. The room-temperature EPR spectrum of **1**·THF in DMSO solution consists of eight sharp lines as expected from the coupling of the one electron spin with that of the  $^{51}\text{V}$  nucleus ( $I = 7/2$ ). The average  $g$  value is 1.981(2) and a second order perturbation effect leads to a non-uniform line spacing between the components (68–78 G), the same as for complex  $[\text{V}(\text{Cp})_2(\text{acac})](\text{CF}_3\text{SO}_3)$  [9]. The average hyperfine coupling constant ( $A$ ), calculated using the equation given by Pake and Rogers [20], is  $67.8 \times 10^{-4} \text{ cm}^{-1}$ , very similar to the values reported for  $[\text{V}(\text{Cp})_2\text{L}_2]$  complexes ( $L = \text{monodentate ligand}$ ) [21]. This result indicates that in **1**·THF the single unpaired electron is in an orbital essentially localized on the  $\text{V}^{\text{IV}}$  center [3,9]. It should be recalled at this point that the EPR sample was exclusively in the liquid phase ( $25\text{ }^{\circ}\text{C}$ ). Under these conditions the anisotropy of the hyperfine and  $g$ -tensors averages due to fast molecular tumbling and the spectrum consists of  $2I + 1$  lines centered at  $g_{\text{ave}}$  and spaced by roughly  $A_{\text{ave}}$  [22].

A characteristic feature in the IR spectrum of **1**·THF is the appearance of a medium intensity band at  $3280 \text{ cm}^{-1}$  assignable [23] to  $\nu(\text{OH})$  of the coordinated  $\text{H}_2\text{O}$  molecules. The broadness and relatively low wavenumber of this band are both indicative of hydrogen bonding. The IR spectra of  $\pi$ -bonded cyclopentadienyl metal complexes have been studied in detail [12–14,24,25]. The bands at 3094, 1444, 1034, 822 and  $578 \text{ cm}^{-1}$  can be assigned to the  $\nu(\text{CH})$ ,  $\nu(\text{CC})$ ,  $\delta(\text{CH})$  [overlapping with the  $\nu_1(A_1)$  mode],  $\nu(\text{CS})$ , of the triflate anion,  $\pi(\text{CH})$  and  $\delta(\text{CCC})$  vibrational modes, respectively. The  $\text{CF}_3\text{SO}_3^-$  ion has been the subject of numerous IR studies to establish a correlation between vibrational frequencies and the mode of coordination [26–29]. Much attention has been given

**Table 2**  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^{\circ}$ ) for complex **1**·THF.

V–O(1W)	2.058(1)	V–C(7)	2.285(8)
V–O(2W)	2.072(2)	V–C(8)	2.288(5)
V–C(1)	2.288(2)	V–C(9)	2.286(5)
V–C(2)	2.257(2)	V–C(10)	2.274(4)
V–C(3)	2.291(2)	V–Cp <sup>b</sup>	1.958
V–C(4)	2.297(2)	Mean C–C <sup>c</sup>	1.401(7)
V–C(5)	2.297(2)	Mean C–S <sup>d</sup>	1.801(3)
V–Cp <sup>a</sup>	1.950	Mean C–F <sup>d</sup>	1.319(3)
V–C(6)	2.282(4)	Mean S–O <sup>d</sup>	1.438(2)
O(1W)–V–O(2W)	81.7(1)	Cp <sup>a</sup> –V–Cp <sup>b</sup>	133.1(2)
O(1W)–V–Cp <sup>a</sup>	109.0(2)	Aver. C–C–C <sup>c</sup>	108.0(5)
O(1W)–V–Cp <sup>b</sup>	106.6(2)	Aver. F–C–F <sup>d</sup>	107.5(2)
O(2W)–V–Cp <sup>a</sup>	106.9(2)	Aver. O–S–O <sup>d</sup>	115.0(1)
O(2W)–V–Cp <sup>b</sup>	107.6(2)	Aver. F–C–S <sup>d</sup>	111.4(2)

<sup>a</sup> Cp is the C(1)C(2)C(3)C(4)C(5) cyclopentadienyl ring centroid.

<sup>b</sup> Cp' is the C(6)C(7)C(8)C(9)C(10) cyclopentadienyl ring centroid.

<sup>c</sup> These values refer to the Cp and Cp' rings.

<sup>d</sup> These values refer to the  $\text{CF}_3\text{SO}_3^-$  counterions.

especially to the  $1300\text{--}1200 \text{ cm}^{-1}$  region and it was proposed that splitting of the  $\nu_{\text{as}}(\text{S–O})$  band is due to coordination in monodentate or bidentate fashions. The  $\text{CSO}_3$  part of the free anion has a  $\text{C}_{3v}$  point group symmetry. In this symmetry, two  $\text{SO}_3$  stretching modes,  $\nu_4(E)$  and  $\nu_2(A_1)$ , and two  $\text{SO}_3$  deformation modes,  $\nu_3(A_1)$  and  $\nu_5(E)$ , are expected [27]. In the IR spectrum of **1** THF, the bands at 1256, 766, 646 and  $520 \text{ cm}^{-1}$  are assigned [27] to the  $\nu_4(E)$ ,  $\nu_2(A_1)$ ,  $\nu_3(A_1)$  and  $\nu_5(E)$  modes, respectively. The number of the bands indicate no evidence for reduction in symmetry below  $\text{C}_{3v}$ , indicating the ionic character of  $\text{CF}_3\text{SO}_3^-$ ; splitting of the modes, due to lowering of the symmetry to  $\text{C}_s$ , would be expected if monodentate or bidentate sulfonate coordination had occurred. The band at  $1178 \text{ cm}^{-1}$  most probably has a predominant C–F stretching character [26].

#### 3.2. Description of structure

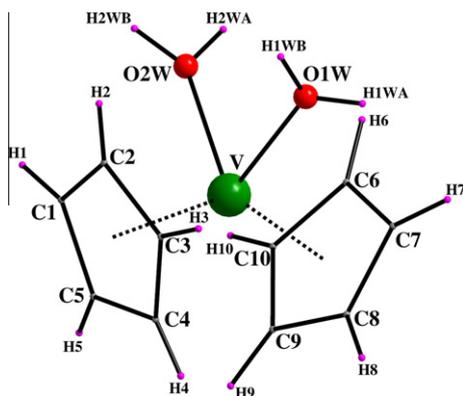
Selected bond lengths and angles for complex **1**·THF are listed in Table 2, while parameters for the hydrogen bonding interactions are summarized in Table 3. The molecular structure of the cation  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]^{2+}$  is shown in Fig. 1 and a small portion of one zig-zag chain present in the crystal structure of the complex is depicted in Fig. 2.

Complex **1**·THF crystallizes in the monoclinic space group  $P2_1/n$ . Its structure consists of well-separated  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]^{2+}$  cations,  $\text{CF}_3\text{SO}_3^-$  anions and lattice THF molecules; the latter will not be further discussed. That the relatively “hard acid”  $[\text{V}(\text{Cp})_2]^{2+}$  moiety prefers to bind to water and not triflate may be consistent with the HSAB model, in that  $\text{H}_2\text{O}$  is most probably a better “hard base” than  $\text{CF}_3\text{SO}_3^-$  [10]. The  $\text{V}^{\text{IV}}$  center adopts the familiar “bent sandwich” geometry found in numerous  $\text{V}(\text{Cp})_2$ -containing complexes [2,9,10,30–32], being  $\pi$ -bonded to two  $\eta^5$   $\text{Cp}^-$  ligands and  $\sigma$ -bonded to two  $\text{H}_2\text{O}$  molecules. If the ring centroids are considered as coordination sites, the coordination polyhedron of the metal ion is a distorted tetrahedron, the other two coordination sites being occupied by the aqua ligands. The  $\text{C}_5\text{H}_5^-$  ligation shows unexceptional metrical parameters. The average C–C distance [1.401(7)  $\text{\AA}$ ], V–C distance [2.285(8)  $\text{\AA}$ ], V-centroid distance [1.954  $\text{\AA}$ ] and centroid–V–centroid angle [133.1(2) $^{\circ}$ ] compare favorably with the corresponding metrical parameters in closely related molecules and cations [2,9,10,30–32]. The dihedral angle between the two  $\text{Cp}^-$  rings is  $46.6^{\circ}$ . The V–O bond lengths in **1** THF [mean value: 2.065(2)  $\text{\AA}$ ] are typical for  $\text{V}^{\text{IV}}\text{--OH}_2$  bonds [33,34] and can be compared, for example, with the average distance of 2.074(3)  $\text{\AA}$  observed in  $[\text{V}_2\text{O}_2\text{F}_6(\text{H}_2\text{O})_2]^{2-}$  [34]. The metrical parameters for the

**Table 3**  
Hydrogen bonding interactions in the crystal structure of **1**·THF.

Interaction <sup>a</sup>	D...A (Å)	H...A (Å)	D–H...A (°)	Symmetry operator of A
O(1W)–H(1WA)···O(14)	2.726	1.911	172.0	$-x, 1-y, -z$
O(2W)–H(2WA)···O(12)	2.625	1.925	167.6	$-1+x, y, z$
O(2W)–H(2WB)···O(16)	2.722	1.821	174.4	$1/2-x, 1/2+y, 1/2-z$

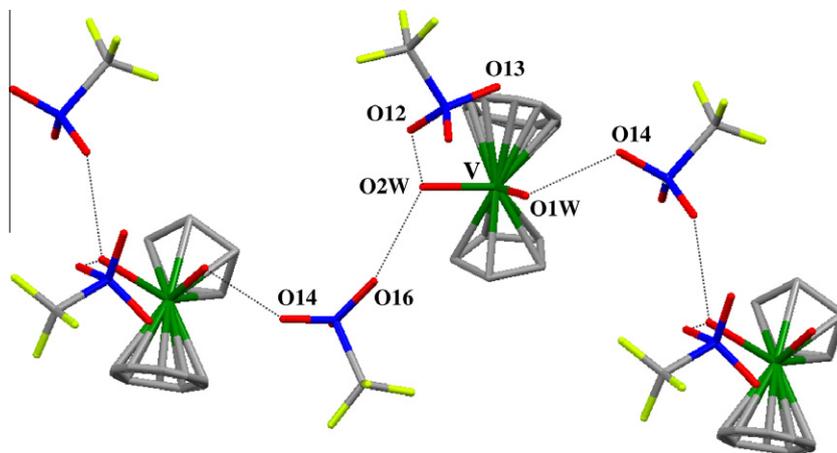
<sup>a</sup> Atoms O(12), O(14) and O(16) belong to the two  $\text{CF}_3\text{SO}_3^-$  counterions. A = acceptor; D = donor.



**Fig. 1.** Labeled PovRay representation of the cation  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]^{2+}$  of complex **1**·THF with the atom numbering scheme. Colour scheme:  $\text{V}^{\text{IV}}$ , olive green; O, red; C, gray; H, purple. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\text{CF}_3\text{SO}_3^-$  groups are typical for the uncoordinated triflate anion [26,28,35]. They adopt a staggered-ethane configuration about the S–C bond; as in other structures containing ionic triflates, the O–S–O [average:  $115.0(1)^\circ$ ] and F–C–S [average:  $111.4(2)^\circ$ ] angles are greater than  $109^\circ$ , while the F–C–F [average:  $107.5(2)^\circ$ ] and O–S–C [average:  $103.2(1)^\circ$ ] are less than  $109^\circ$ .

Two oxygen atoms of one triflate anion [O(14), O(16)] participate in hydrogen bonds to vanadium-bound water molecules [O(1W), O(2W)] from two different  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]^{2+}$  cations, producing an infinite, zig-zag chain throughout the crystal lattice (Fig. 2). Their parameters are in the range of hydrogen bonds of medium strength. Atom O(2W) also acts as a hydrogen bond donor to an oxygen atom [O(12)] of the second triflate anion, thus providing a third indirect binding of the  $\text{V}^{\text{IV}}$  atom to the triflate groups via a water bridge. Finally, one of the bound water molecules [O(1W)] forms a weak hydrogen bond with the heavily disordered oxygen atom of the THF solvate molecule.



**Fig. 2.** Capped stick representation of one 1D zig-zag chain created by hydrogen bonds in the crystal structure of **1**·THF. Colour scheme:  $\text{V}^{\text{IV}}$ , olive green; O, red; C, gray; S, blue; F, yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 4**  
Selected structural parameters for the cations of complexes  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]\{\text{O}_2\text{P}(\text{OPh})_2\}_2$  [9]<sup>a</sup> and **1**·THF.

Parameter <sup>b</sup> (Å) or (°)	$[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]\{\text{O}_2\text{P}(\text{OPh})_2\}_2$	<b>1</b> ·THF
V–O <sub>water</sub>	2.050	2.065
V–Cp	1.963	1.954
V–C	2.297	2.285
C–C	1.402	1.401
O–V–O	84.2	81.7
Cp–V–Cp	133.0	133.1

<sup>a</sup> The crystal structure of this complex is composed of two crystallographically independent mononuclear cations and the parameters of both cations have been taken into account for the comparison.

<sup>b</sup> All values, except the O–V–O and Cp–V–Cp angles for **1**·THF, are mean values.

Complex **1**·THF is the second structurally characterized complex containing the cation  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]^{2+}$ ; the first one is  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]\{\text{O}_2\text{P}(\text{OPh})_2\}_2$  [10] mentioned in the introduction. The molecular structures of the pseudotetrahedral cations of the two compounds are very similar. Rather than discuss similarities, we list in Table 4 typical structural parameters for the cations of the two complexes. The remarkable similarity of the molecular structures is clearly evident. Obviously, the replacement of  $\text{CF}_3\text{SO}_3^-$  by  $(\text{OPh})_2\text{PO}_2^-$  has no effect on the structure of the cations.

#### 4. Concluding comments and perspectives

The present work extends the body of results that emphasize the fact that the reactivity chemistry of the compounds  $[\text{M}(\text{Cp})_2\text{X}_2]$  (M = Ti, Zr, Hf, V; X = halide or pseudohalide) can lead to interesting products. Compound **1**·THF, described in this work, is only the second complex containing the cation  $[\text{V}(\text{Cp})_2(\text{H}_2\text{O})_2]^{2+}$ . From the synthetic inorganic chemistry viewpoint, we have further developed the use [35–37] of the THF-soluble salt  $\text{Ag}(\text{CF}_3\text{SO}_3)$  for the preparation of  $\text{M}^{\text{IV}}/\text{Cp}^-$  complexes containing coordinated [35,36] or purely ionic [34] triflates.

As far as future perspectives are concerned, we currently try to use **1**·THF as a convenient starting material for reactions with bridging organic ligands, including diols [38,39] and 2-pyridyl oximes [40], in an attempt to synthesize mixed organometallic/coordination clusters of V. We are also performing reactions between **1**·THF or  $[V(Cp)_2Cl_2]$  (the “metal”) and mononuclear  $Ni^{II}$  or  $Co^{II}$ /2-pyridyl oximate complexes containing free oxygen sites (the “ligand”) [41] for the synthesis of V/Co and V/Ni clusters using the “metal complexes as metals and metal complexes as ligands” approach. Finally, we plan to study the cytotoxic activity of **1**·THF.

## Appendix A. Supplementary material

CCDC 883853 contains the supplementary crystallographic data for **1** THF. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2012.09.038>.

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