

Synthesis, characterization and structural investigation of the first vanadocene(IV) carboxylic acid complexes prepared from the vanadocene dichloride

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Abstract

Two types of vanadocene complexes with carboxylic acids have been synthesized from the aqueous solution, $\text{Cp}_2\text{V}(\text{OOCR})_2$ ($\text{R} = \text{H}, \text{CCl}_3$ and CF_3) and $\text{Cp}_2\text{V}(\text{OOC}-\text{A}-\text{COO})$ ($\text{A} = -$ and CH_2), and characterized by EPR, IR, and Raman spectroscopy and X-ray diffraction analysis. Monocarboxylic and dicarboxylic acids form monodentate and chelate complexes, respectively. Both bonding types were evidenced by X-ray diffraction analysis. Structures and EPR HFC tensors were also calculated at the DFT level. Correlation between the complex structure and HFC tensor was established. HFC tensors are characteristic for the type of bond of carboxylic acid on vanadocene fragment. It is shown that the structure of complexes can be determined by the combination of theoretical method with experimental EPR spectra.

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1. Introduction

The disubstituted metallocene derivatives are known as “bent-sandwich” complexes, where bis-cyclopentadienyl moieties is η^5 -carbon-metal bonded and positioned in a bent conformation with respect to the central metal atom [1–8]. Such metallocenes containing transition metals in oxidation state IV exhibit antitumor properties both *in vivo* and *in vitro*. In contrast to cisplatin their side effect are much lower [9,10].

The neutral dihalo complexes, e.g., Cp_2TiCl_2 and Cp_2VCl_2 , have emerged as promising alternatives to cisplatin [11]. Because the interaction between the central metal atom and its coordinating ligands contributes to the redox properties of metallocenes [12] as well as to

their stability in aqueous solutions [13–15], different ligands have been selected for lead optimization effect.

Some titanocene carboxylate complexes have been tested for antiproliferative activity against Ehrlich ascites tumor in mice [16]. It was shown that the introduction of ligands bearing hydrophilic groups, such as carboxylic group, results in a diminution of the toxic properties, a widening of the therapeutic range, and an increase in the water solubility in comparison with that of titanocene dihalides [16,17]. The interaction of Cp_2VCl_2 (**1**) with carboxylic acids has not been studied yet.

The paramagnetism of the central metal atom d^1 V(IV) and its nuclear spin (^{51}V : $I = 7/2$, abundance 99.8%) make vanadocene(IV) complexes suitable for EPR characterization. The EPR spectra contain information about the coordination environment of the central atom. In particular, the isotropic hyperfine coupling (HFC) constant bears information about the delocalization of unpaired electron between the central atom and ligands.

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Here we report the preparation and structural characterisation of vanadocene complexes of monocarboxylic $\text{Cp}_2\text{V}(\text{OOCR}_2)_2$ ($\text{R}=\text{H}$, CCl_3 , CF_3) and dicarboxylic acids $\text{Cp}_2\text{V}(\text{OOC-A-COO})$ ($\text{A}=\text{—}$, CH_2). Experimentally determined structural and spectroscopic data were compared with the results of DFT calculations, employing the B3PW91 functional. The correlation between coordination compound structure and HFC tensor was investigated.

2. Results and discussion

2.1. Vanadocene(IV) complexes of monocarboxylic acids

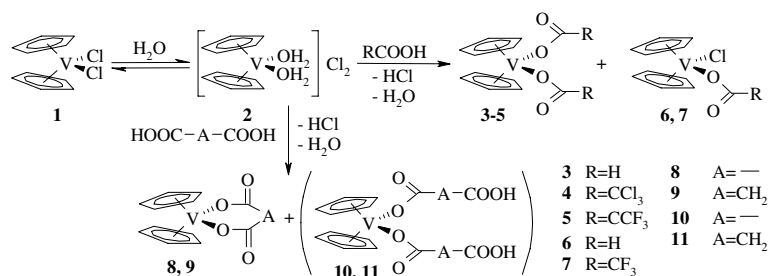
Upon the solvation in aqueous solution the Cp_2VCl_2 (**1**) complex immediately dissociates, splitting off both Cl^- ligands, and it forms vanadocene species $\text{Cp}_2\text{V}(\text{H}_2\text{O})_2^{2+}$ (**2**) (see Scheme 1) [13,14]. No significant changes in the EPR signal can be observed when carboxylic acid is added into the solution. The EPR signal remains the same even after precipitation of chloride ions. After water evaporation and dissolution in inert solvent (CH_2Cl_2), where the charged complex **2** is insoluble [5], the simple eight-line EPR spectra due to a single EPR active species are obtained. These spectra are different from the spectra of the original complex **1** (see Table 1).

Based on the results of elemental analyses, IR and Raman spectroscopy new compounds contain two η^5 -

cyclopentadienyl ligands: stretching $\nu_a(\text{C-H})$ (IR: 3100–3130 cm^{-1} (m)) and $\nu_s(\text{C-H})$ (Raman: 3115–3140 cm^{-1} (s)) and the Cp ring breathing (Raman: $\nu_s(\text{C-C})$ 1130–1135 cm^{-1} , (vs)) are the η^5 -Cp ring vibrational fingerprints (Table 2) [18]. The Raman band at 275–290 cm^{-1} is characteristic for the tilted $[\text{Cp-V-Cp}]^{2+}$ fragment ($\kappa(\text{Cp})$). The presence of two molecules of carboxylic acid (monodentate bond of carboxylic group) is supported by the $\nu_a(\text{COO})$ stretching (IR: 1630–1695 cm^{-1} (vs)) and also by the elemental analyses. In agreement with earlier reports on the coordination behaviour of carboxylic acids with metals the $\nu_a(\text{COO})$ vibrations are shifted to higher wavenumbers compared with the free carboxylic acid ligands [19]. The molecular structure of $\text{Cp}_2\text{V}(\text{OCCCl}_3)_2$ (**4**) was validated by single-crystal X-ray diffraction analysis (see Fig. 1 and Table 3).

The carboxylate complexes **3–5** show very similar HFC tensors. Isotropic HFC constants are in the narrow range of 220–222 MHz (Table 1). Also anisotropic components of HFC tensor (measured in the dilute powders details given in Section 4.2) are similar for complexes **3–5** (with the differences no larger than 4 MHz).

The existence of complexes (**3**, **5**) with two carboxylic ligands is supported by the analyses of compounds obtained upon a partial precipitation of Cl^- ions (Fig. 2). EPR spectrum obtained after partial precipitation of Cl^- ions from aqueous solution of (**1**) and formic acid, followed by evaporation and dissolution in inert solvent (CH_2Cl_2) is depicted in Fig. 2. This spectrum is super-



Scheme 1. Interaction of vanadocene dichloride with carboxylic acids.

Table 1
Comparison of experimental and calculated^a HFC tensors (MHz)

		1	3	4	5	8	9	10	11
A_{iso}	Experimental	−207.2	−220.3	−221.1	−222.2	−189.8	−208.1	—	—
	Calculated	−158.6	−172.2	−174.1	−173.9	−154.0	−166.2	−172.7	−172.3
T_x	Experimental	−11.0	−16.2	−16.1	−19.4	−52.0	−47.0	—	—
	Calculated	−2.2	1.7	−2.7	−3.6	−56.6	−50.8	−3.1	1.4
T_y	Experimental	−140.0	−148.4	−145.1	−145.0	−117.3	−126.0	—	—
	Calculated	−138.1	−145.4	−141.3	−140.8	−103.2	−109.9	−141.2	−145.4
T_z	Experimental	151.0	164.6	161.2	164.4	169.4	173.0	—	—
	Calculated	140.3	143.7	144.0	144.4	159.8	160.7	144.3	144.0
$\langle S^2 \rangle^b$	Calculated	0.7845	0.7819	0.7837	0.7839	0.7779	0.7790	0.7831	0.7821

^a HFC calculated in geometries obtained at the DFT level.

^b Nominal $\langle S^2 \rangle$ value for a doublet is 0.7500.

Table 2
Characteristic infrared and Raman absorptions (cm^{-1}) and assignments for vanadocene complexes

		$\nu_a(\text{C-H})\text{Cp}$	$\nu_s(\text{C-H})\text{Cp}$	$\nu_a(\text{COO})$	$\nu_s(\text{C-C})\text{Cp}$	$\delta(\text{CH})\text{Cp}$	$\kappa(\text{Cp})$	$\tau(\text{Cp})$
3	IR	3103 (m)		1632(vs)		835(s)		
	Raman		3130(s)		1131(vs)		290(vs)	85(vs)
4	IR	3104(m)		1681(vs)				
	Raman		3131(s)	1685(m)	1132(vs)		279(vs)	85(vs)
5	IR	3126(m)		1691(vs)		837(s)		
	Raman		3131(s)	1685(m)	1132(vs)	841(m)	279(vs)	85(vs)
8	IR	3101(m)		1696(vs)		837(s)		
	Raman		3115(s)	1679(vs) 1695(w) 1678(w)	1131(vs)	829(m)	286(vs)	86(m)
9	IR	3102(m)		1739(vs) 1715(vs)	847(s)			
	Raman		3120(m)	1695(w) 1678(w)	1132(vs)	829(m)	280(vs)	85(vs)

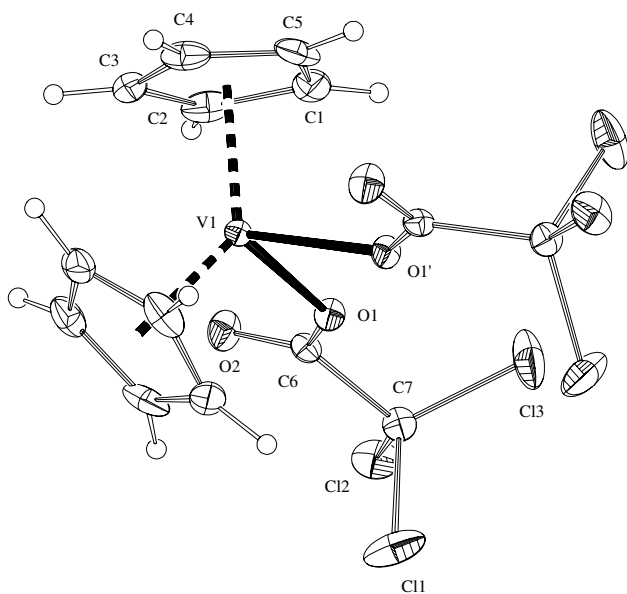


Fig. 1. ORTEP drawings of the molecular structures of complex **4** with atom numbering of symmetrically independent part. The second part of molecule is related by rotation around the twofold axes along *b*. (ellipsoids: 30% probability).

Table 3
Selected bond lengths (\AA) and bond angles (deg) of some vanadocene complexes determined from X-ray diffraction analyses

	1 ^a	4	8
V–X1 ^b	2.409(2)	2.0313(15)	2.0208(9)
V–X2 ^b	2.410(2)	2.0313(15)	2.0379(8)
V–Cg1 ^c	1.97(1)	1.9608(12)	1.9591(7)
V–Cg2 ^c	1.98(1)	1.9608(12)	1.9615(6)
X1–V–X2 ^b	87.1(1)	77.64(8)	78.55(3)
Cg1–V–Cg2 ^c	132.1(5)	133.31(6)	133.49(3)

^a Molecule B in the unit cell [1].

^b X1, X2 – chlorine atoms (oxygen atoms, respectively) bonded to the vanadium atom.

^c Cg – the centroid of the cyclopentadienyl ring.

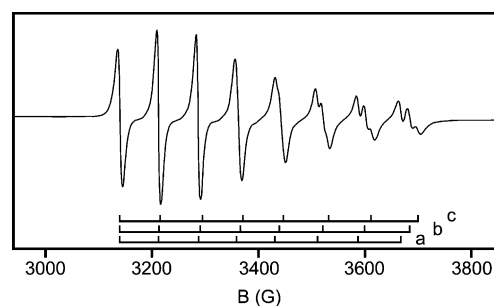


Fig. 2. EPR spectra of a sample isolated from the reaction mixture (Cp_2VCl_2 and HCOOH) upon the partial precipitation of chloride ions. Spectrum is a superposition of the spectra of three vanadocene complexes: (a) Cp_2VCl_2 (**1**), (b) $\text{Cp}_2\text{V}(\text{OOCH})\text{Cl}$ (**6**) and (c) $\text{Cp}_2\text{V}(\text{OOCH})_2$ (**3**).

position of simple eight-line spectra of reactant (**1**, Fig. 2(a)), singly substituted complexes with one carboxylic acid ligand (**6**, Fig. 2(b)), and complexes with both chlorine ligands substituted by carboxylic acids (**3**, Fig. 2(c)). Monosubstituted carboxylate complex **6** shows EPR parameters ($A_{\text{iso}} = 213.2$ MHz; $g_{\text{iso}} = 1.9803$) that are mean value of these parameters for complexes **1** and **3**. The same results were obtained for complexes **5** and **7** (EPR parameters of **7**: $A_{\text{iso}} = 215.1$; $g_{\text{iso}} = 1.9805$). The EPR parameters of complexes **3** and **5** are very close to those of $\text{Cp}_2\text{V}(\text{H}_2\text{O})_2^{2+}$ (**2**). Therefore, it is not clear whether the water ligands are exchanged by carboxylic ligands already in the liquid phase.

From the EPR spectra it is evident that the substitution of H by CCl_3 group does not change significantly HFC tensor. The changes of spin density on central V^{4+} cation due to the electron withdrawing CF_3 group were studied for $\text{Cp}_2\text{V}(\text{OOC}\text{CF}_3)_2$ (**5**) complex. However, almost no change in HFC tensor was observed. Either the spin density in the central atom is not influenced by

CF₃ group or the changes in spin density are compensated by the partial bond polarization.

Based on the results of EPR analysis we conclude that A_{iso} and T_x , T_y , and T_z parameters are very similar for any complex of carboxylic acid with monodentate bond on [Cp₂V]²⁺ cation.

2.2. Vanadocene(IV) complexes with dicarboxylic acids

Vanadocene dichloride interacts in aqueous solution with both, oxalic and malonic acids. Formation of chelate complexes is evidenced from results of elemental analyses and from splitting of $\nu_a(\text{COO})$ in infrared spectra [20]. The presence of two η^5 -bonded cyclopentadienyl rings is evidenced from vibrational spectra ($\nu_s(\text{C-H})$, $\nu_a(\text{C-H})$, $\nu_s(\text{C-C})$, $\kappa(\text{Cp})$; see Table 2) [18].

The structure of complex **8** was determined by single-crystal X-ray diffraction. This compound forms dimer in the solid state with two Cp₂V(OOC)₂ units connected via the oxalic acid bridge (Fig. 3).

The chelate bonding can be also evidenced in the EPR spectra. The interaction of complex **2** with dicarboxylic acid is rather different than the interaction with monocarboxylic acid. The EPR spectra are changed immediately upon the mixing of aqueous solution of **1** with dicarboxylic acid. Original simple eight-line EPR spectrum changes to the spectra corresponding to two paramagnetic compounds. With the increased amount of dicarboxylic acid the intensity of the spectrum which is characteristic for complex **2** decreases while the intensity of the spectrum of new compound increases. It is reasonable to interpret these changes of EPR spectra as an evidence of formation of the complex with chelate bond with carboxylic acid right in the aqueous solution. Isolated complexes of dicarboxylic acids **8** and **9** show different A_{iso} , T_x , T_y , and T_z parameters than those measured for complexes of monocarboxylic acids (**3–5**).

We believe that the difference in HFC tensors is due to the different bonding on the central atom. Complexes of mono- and dicarboxylic acids can be clearly distinguished from A_{iso} , T_x and T_y parameters (see Table 1). Isotropic HFC constant increases with the increased size of the chelate ring and it approaches HFC constant obtained for the monocarboxylic acids.

2.3. Calculations

Experimental and calculated HFC tensors are summarized in Table 1. Calculations were carried out at the B3PW91 level of theory at the geometries optimized at the same level. For Cp₂VCl₂ (**1**) [1], Cp₂V(OOCCl₃)₂ (**4**) and Cp₂V(OOC)₂ (**8**) complexes where experimental structures are known the HFC tensors were calculated also at the experimental geometries (Table 5); EPR parameters are almost identical for both sets of geometries. This is essential for finding the correlation between structure and HFC tensors. Calculated isotropic HFC constants are systematically underestimated to experimental values by 19–23%. Similar trend was observed for various vanadium(IV) complexes and it depends on the exchange-correlation functional and basis set used [21,22]. Note that this underestimation is systematic and that it is the same for both complexes with monodentate ligands (**1**, **3**, **4**, **5**) and complexes with chelate ligand (**8**, **9**). It is clear that the anisotropic part of HFC tensor (A_x , A_y , and A_z) must be underestimated by the same amount as isotropic HFC constant. With a different exchange-correlation functional and larger basis set the agreement with experiment could be improved [21]. The use of an exchange-correlation functional with larger component of exact exchange (e.g., BHPW91) leads to the decrease of A_{iso} , thus the better agreement between calculated and experimental values is reached. However, the use of such functional is associated with significantly

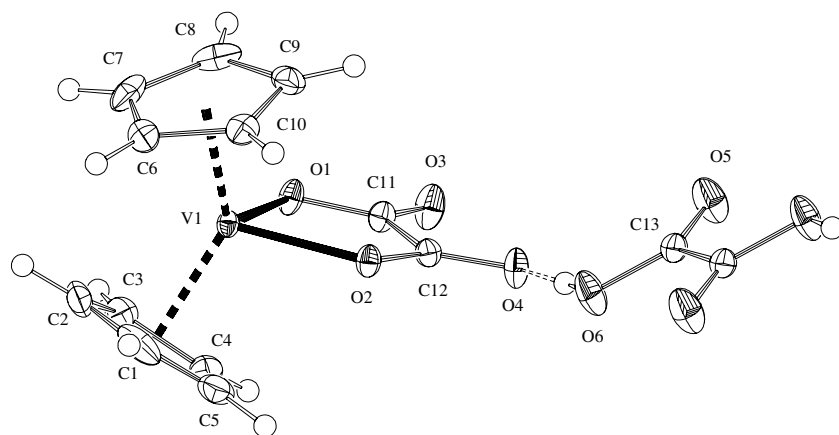


Fig. 3. ORTEP drawings of the molecular structures of complexes **8** with atom numbering of symmetrically independent part. The second part of solvate is related by center of symmetry. (ellipsoids: 50% probability). Hydrogen bond is drawn as dashed line (O6...O4 2.586(1)Å, O6–H6A...O4 178(2)°).

larger spin-contamination. Thus, the better agreement of calculated A_{iso} is compensated by the partial loss of reliable description of relative A_{iso} for various complexes (spin-contamination is not the same for all studied complexes). A similar behavior was reported for other transition metal compounds by Munzarova and Kaupp [21]. Therefore, we decided to report results obtained with B3PW91 exchange-correlation functional.

For dicarboxylic acids we have optimized the geometries of both structure types, with a chelate bonding (**8**, **9**) and with monodentate bonding (**10**, **11**). For complexes with monodentate bonds the calculated HFC tensors are in the same range as found for complexes of monocarboxylic acids **3–5**. For complexes with chelate bond the parameters A_{iso} and T_y are lower and parameter T_x higher in agreement with experimental observation. In agreement with experimental EPR spectra the calculated values of A_{iso} parameter of chelate complexes increases with the increase of the chelate ring. Thus, the DFT calculations of HFC tensor provide further support for the experimentally observed formation of chelate bonded dicarboxylic acids complexes with vanadocene.

2.4. Crystal structures

The X-ray structures of the complexes **4** and **8** are shown in Figs. 1 and 3. Selected distances and bond angles are given in the Table 3 and the crystallographic data are presented in Table 4. Molecules **4** and **8** have the typical bent metallocene structure in which the two η^5 -bonded Cp rings and two oxygen atoms of monodentate bonded trichloroacetic acids (**4**) or chelate bonded oxalic acid (**8**) occupy the pseudotetrahedral coordination sites around the vanadium(IV) center. A rigorous overall C_2 molecular symmetry was found for complex **4**.

The V-ring centroid distance is 1.96 Å (**4**, **8**), the ring centroid-V-ring centroid angles are 133.3° (**4**) and 133.5° (**8**). These values are consistent with corresponding distances and angles found in the related vanadocene(IV) complexes (V-centroid distance 1.96–1.97 Å, centroid-V-centroid angle 131.2–134.8°) [1,3–5,23].

The V–O bond distances in **4** (2.031 Å) and **8** (2.021, 2.038 Å) are comparable with corresponding distance found in $\text{Cp}_2\text{V}(\text{OH}_2)_2 \cdot 2\text{O}_2\text{P}(\text{OPh})_2$ (2.029–2.067 Å) [5] and slightly longer than in $[\text{Cp}_2\text{V}(\text{acac})](\text{OTf})$ (1.996–2.001 Å) [4] and slightly shorter than in vanadocene(III) complex $\text{Cp}_2\text{V}(\text{OOC}_6\text{H}_4\text{OH})$ (2.055 Å) [24]. The O–V–O angles in **4** (77.6°) and **8** (78.6°) are smaller than that found in $\text{Cp}_2\text{V}(\text{OH}_2)_2 \cdot 2\text{O}_2\text{P}(\text{OPh})_2$ (83.9°; 84.4°) [5] and $[\text{Cp}_2\text{V}(\text{acac})](\text{OTf})$ (87.0°) [4].

The V–O distances are slightly shorter than the Ti–O distances (1.95–1.98 Å) reported for $\text{Cp}_2\text{Ti}(\text{OOCR})_2$ (R = H, CF_3) [6,7] and $\text{Cp}_2\text{Ti}(\text{OOC})_2$ (2.00 Å) [8].

Table 4
Crystal data of **4** and **8**, measurement and refinement details^a

Compound	4	8
Formula	$\text{C}_{14}\text{H}_{10}\text{Cl}_6\text{O}_4\text{V}$	$\text{C}_{12}\text{H}_{10}\text{O}_4\text{V} \cdot 0.5(\text{C}_2\text{H}_2\text{O}_4)$
Crystal system	Orthorhombic	Monoclinic
Space group	$C22_1$ (No. 20)	$C2/c$ (No. 15)
a (Å)	10.6390(2)	21.5970(4)
b (Å)	13.8440(3)	8.3620(2)
c (Å)	13.1060(3)	15.4580(3)
β (°)		120.3011(9)
Z	4	8
V (Å ³)	1930.33(7)	2410.25(9)
D_c (g cm ⁻³)	1.741	1.732
Crystal size (mm)	$0.5 \times 0.125 \times 0.1$	$0.27 \times 0.27 \times 0.25$
μ (mm ⁻¹)	1.360	0.847
h range	–13,13	–27,28
k range	–17,17	–10,10
l range	–16,16	–20,19
Reflections measured	14,561	18,857
– independent (R_{int}^a)	2214(0.027)	2738(0.023)
– observed [$I > 2\sigma I$]	2146	2517
No. of parameters	115	185
GOF ^b	1.061	1.051
R^c , wR^c	0.030, 0.072	0.026, 0.077
$\Delta\rho$ (e Å ⁻³)	0.721, –0.555	0.386, –0.435

$$^a R_{\text{int}} = \sum |F_o^2 - F_{o,\text{mean}}^2| / \sum F_o^2.$$

$$^b \text{GOF} = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diffs}} - N_{\text{params}})]^{1/2} \text{ for all data.}$$

$$^c R(F) = \sum ||F_o| - |F_c|| / \sum |F_o| \text{ for observed data, } wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2} \text{ for all data.}$$

3. Conclusions

Vanadocene dichloride (**1**) interacts with carboxylic acids forming the carboxylate complexes. Two types of complexes differing in the type of bond on the central V^{4+} cation were isolated from the aqueous solution: (I) vanadocene dichloride forms complexes with two monodentate bonded molecules of carboxylic acids (II) vanadocene dichloride forms complexes with single chelate bonded molecule of dicarboxylic acid. Both bonding types were evidenced by X-ray diffraction analyses. Different bonding types show rather different HFC tensors. The structures and HFC tensors were also calculated at the density functional level of theory. The correlation between the structure and HFC tensors was clearly shown. It is shown that the structure of complexes can be determined by the combination of theoretical method with experimental EPR spectra. This is of particular importance for the complexes where X-ray diffraction analysis cannot be performed due to the low stability of the complex and difficulties in its isolation.

4. Experimental

4.1. Methods and materials

All reactions and manipulations were performed under an inert atmosphere of argon with use of the stan-

dard Schlenk techniques. Water was deionized, double distilled and thoroughly saturated with argon. Another solvents were dried by standard methods and saturated with argon. Purity of prepared complexes was checked by EPR, IR and Raman spectroscopy.

4.2. Spectral measurements

EPR spectra were recorded on the ERS 221 (WG Berlin) spectrometer at X-band. Isotropic spectra were measured in solutions (CH_2Cl_2 , DMSO or water) at ambient temperature. They exhibited the expected eight lines caused by interaction of the unpaired electron with ^{51}V ($I = 1/2$; 99.8%) nucleus. The anisotropic spectra were obtained from dilute powders (in diamagnetic matrix of related titanocene complex) or from frozen solutions (CHCl_3 or DMSO) at liquid-nitrogen temperature. They showed two well resolved sets of hyperfine features. The third sets were calculated from equations $g_{\text{iso}} = 1/3(g_x + g_y + g_z)$ and $A_{\text{iso}} = 1/3(A_x + A_y + A_z)$.

Spectra obtained were simulated using EPR simulation software SimFonia v.1.2 (Bruker). Second-order perturbation theory for interaction of unpaired electronic spin with vanadium nuclear spin, anisotropic linewidths and mixed Lorentzian/Gaussian lineshapes were used.

IR spectra were recorded at 4000–350 cm^{-1} region on a Perkin–Elmer 684 using Nujol mulls between KBr windows. Raman spectra were recorded on a Bruker IFS 55s with extension FRA 106 at 50–3500 cm^{-1} .

4.3. Preparation of compounds

All carboxylate complexes (**3–5**, **8**, **9**) were prepared by reactions of Cp_2VCl_2 (**1**) with carboxylic acid in aqueous solution. Cp_2VCl_2 (**1**) was prepared from vanadium tetrachloride and sodium cyclopentadienide in benzene by the standard method [25]. $\text{Cp}_2\text{Ti}(\text{OOCH})_2$, $\text{Cp}_2\text{Ti}(\text{OOCFF}_3)_2$ and $\text{Cp}_2\text{Ti}(\text{OOCCL}_3)_2$, which were used for dilute powder EPR measurements, were prepared following the methods described elsewhere [6,7,16].

4.3.1. Synthesis of $\text{Cp}_2\text{V}(\text{OOCH})_2$ (**3**), and $\text{Cp}_2\text{V}(\text{OOCFF}_3)_2$ (**5**)

0.5 g (1.98 mmol) of Cp_2VCl_2 was dissolved in 40 ml formic acid (98%) and 12 ml trifluoroacetic acid (25%) respectively. 1.15 g (5 mmol) Ag_2O was added into this solution and formed suspension was stirred for 10 min. The suspension was filtrated and the filtrate was evaporated to dryness. The formed green solid was extracted with 10 ml CH_2Cl_2 and the filtrate was precipitated with 20 ml of hexane. The product was decanted, twice washed with 10 ml hexane and dried in vacuo.

Complex $\text{Cp}_2\text{V}(\text{OOCH})_2$ (**3**). Yield: 0.26 g; 0.96 mmol; 48.4%; Calc. for $\text{C}_{12}\text{H}_{12}\text{O}_4\text{V}$ (MW 271.16): C,

53.15; H, 4.46. Anal. Found: C, 52.90; H, 4.50. EPR: CH_2Cl_2 solution $A_{\text{iso}} = 79.46$ G, $g_{\text{iso}} = 1.981$, DMSO solution $A_{\text{iso}} = 79.02$ G, $g_{\text{iso}} = 1.981$; dilute powder $A_x = 134.7$ G, $A_y = 85.0$ G, $A_z = 18.7$ G, $g_x = 1.956$, $g_y = 1.988$, $g_z = 2.000$; IR (KBr, nujol mull): 3103 (m), 2809(m), 2709(m), 1632(vs), 1445(m), 1284(vs), 1025(m), 893(m), 835(s); 758(m) 453(w); Raman: 3130(s), 2810(m), 1449(m), 1378(s), 1131(vs), 434(m), 342 (vs), 290(vs), 222(m), 185(m), 85(vs).

Complex $\text{Cp}_2\text{V}(\text{OOCFF}_3)_2$ (**5**). Yield: $\text{Cp}_2\text{V}(\text{OOCFF}_3)_2$ 0.45 g; 1.11 mmol; 55.8%. Calc. for $\text{C}_{14}\text{H}_{10}\text{F}_6\text{O}_4\text{V}$ (MW 407.16): C, 41.30; H, 2.47. Anal. Found: C, 41.10; H, 2.40. EPR: CH_2Cl_2 solution $A_{\text{iso}} = 80.16$ G, $g_{\text{iso}} = 1.981$; dilute powder $A_x = 134.3$ G, $A_y = 86.9$ G, $A_z = 19.2$ G, $g_x = 1.953$, $g_y = 1.987$, $g_z = 2.003$; IR (KBr, nujol mull): 3126(m), 1691(vs), 1414(m), 1378(vs), 1203(vs), 1191(s), 1140(s), 1017(m), 837(s), 790(m), 724(s), 610(m), 522(m); Raman: 3140(m), 1132(vs), 841(m), 352(m), 305(m), 286(vs), 85(vs).

4.3.2. Synthesis of $\text{Cp}_2\text{V}(\text{OOCCL}_3)_2$ (**4**)

0.5 g (1.98 mmol) of Cp_2VCl_2 (**1**) was dissolved in 10 ml water. 8 mmol of trichloroacetic acid was added to the solution. The formed suspension was stirred for 10 min, decanted and washed twice with 20 ml water.

$\text{Cp}_2\text{V}(\text{OOCCL}_3)_2$ (**4**). Yield: 0.71 g; 1.40 mmol; 70.9%; Calc. for $\text{C}_{14}\text{H}_{10}\text{Cl}_6\text{O}_4\text{V}$ (MW 505.86): C, 33.23; H, 1.99; Cl, 42.05. Anal. Found: C, 33.00; H, 2.00; Cl, 42.10. EPR: CH_2Cl_2 solution $A_{\text{iso}} = 79.75$ G, $g_{\text{iso}} = 1.981$; dilute powder $A_x = 134.0$ G, $A_y = 85.3$ G, $A_z = 19.9$ G, $g_x = 1.953$, $g_y = 1.987$, $g_z = 2.005$; IR: 3104(m), 1681(vs), 1337(s), 1318(s), 1015(m) 949(m), 834(s); 742(s), 685(s), 544(m), 512(m); Raman: 3131(s), 1685(m), 1132(vs), 433(vs), 335 (m), 279(vs), 168(m), 85(vs). Suitable crystals for X-ray diffraction analysis were grown from dichloromethane solution.

4.3.3. Synthesis of $\text{Cp}_2\text{V}(\text{COO})_2 \cdot 0.5(\text{COOH})_2$ (**8**)

0.5 g (1.98 mmol) of Cp_2VCl_2 (**1**) was dissolved in 10 ml water. 12 mmol of oxalic acid was added to the solution. The formed suspension was stirred for 10 min, decanted and washed twice with 20 ml acetone.

$\text{Cp}_2\text{V}(\text{OOC})_2 \cdot 0.5(\text{COOH})_2$ (**8**). Yield: 0.42 g; 1.34 mmol; 67.5%. Calc. for $\text{C}_{13}\text{H}_{11}\text{O}_6\text{V}$ (MW 314.16): C, 49.70; H, 3.53. Anal. Found: C, 49.50; H, 3.50. EPR: DMSO solution $A_{\text{iso}} = 68.33$ G; $g_{\text{iso}} = 1.984$; water solution $A_{\text{iso}} = 68.27$ G; $g_{\text{iso}} = 1.984$; frozen DMSO solution $A_x = 111.9$ G, $A_y = 86.6$ G, $A_z = 6.5$ G, $g_x = 1.961$, $g_y = 1.995$, $g_z = 1.997$; IR (KBr, nujol mull): 3101(m), 2537(s), 2447(s), 1727(s), 1696(vs), 1679(vs), 1636(vs), 1623(vs), 1616(vs), 1449(m), 1418(s), 1362(m), 1251(s), 1200(vs), 1129(m), 1027(m), 1017(m), 993(w), 892(m), 859(s), 837(s), 780(s), 693(s), 593(m), 537(m), 488(w), 431(m), 371(m); Raman: 3115(s), 3099(m), 1745(w), 1695(w), 1678(w), 1640(w), 1453(w), 1437(m), 1401(m), 1388(m), 1370(m), $\nu(\text{C}-\text{O})$ 1251(m), 1131(vs), 1077(m),

829(m), 536(m), 443(s), 431(m), 395(m), 309(s), 286(vs), 256(s), 225(m), 206(s), 138(m), 86(m). Suitable crystals for X-ray diffraction analysis were grown from aqueous solution.

4.3.4. Synthesis of $Cp_2V(OOCCH_2COO)$ (**9**)

0.5 g (1.98 mmol) of Cp_2VCl_2 was dissolved in 25 ml (0.48 mol l⁻¹) malonic acid. 1.15 g Ag_2CO_3 was added to the solution. The formed suspension was stirred 10 min and filtrated. The filtrate was evaporated to dryness. The product was extracted with methanol and recrystallized from it.

$Cp_2V(OOCCH_2COO)$ (**9**). Yield: 0.27 g; 0.95 mmol; 48.2%; Calc. for $C_{13}H_{12}O_4V$ (MW 283.17): C, 55.14; H, 4.27. Anal. Found: C, 54.90; H, 4.20. EPR: DMSO solution $A_{iso} = 75.04$ G $g_{iso} = 1.981$; water solution $A_{iso} = 74.01$ G $g_{iso} = 1.981$; IR (KBr, nujol mull): 3102(m), 1739(vs), 1715(vs), 1628(vs), 1556(s), 1324(m), 1302(m), 1192(s), 910(m), 845(s), 639(m), 467(m), 428(m); Raman: 3120 (m), 2997(m), 2957(m), 1451(m), 1132(s), 926(m), 434(m), 306(m), 280(vs), 85(vs).

4.4. X-ray crystallography

The X-ray data for **4** and **8** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and ω scan mode. Data reductions were performed with DENZO-SMN [26]. The absorption was neglected. Structures were solved by direct methods (Sir92) [27] and refined by full matrix least-square based on F^2 (SHELXL 97) [28].

Crystal data are summarized in Table 5. Hydrogen atoms were treated in both structures similarly, those on carbon were calculated into ideal positions, riding during refinement on the respective pivot atom. The isotropic displacement parameters of hydrogen atoms were set to 1.2x U_{eq} of the attached atom. Hydrogen atom on O was found on difference Fourier map and refined isotropically.

The space-group of crystal of complex **4** is noncentrosymmetric, however, from value of chirality parameter it follows, that it is racemic twin with equal ration of two components. Therefore, the correction for twinning was included into refinement.

Table 5
Calculated HFC tensors (MHz) in X-ray geometries

	1	4	8
A_{iso}	-159.9	-175.5	-147.3
T_x	-9.6	-13.9	-56.0
T_y	-132.9	-134.4	-101.4
T_z	142.5	148.3	157.3
$\langle S^2 \rangle^a$	0.7881	0.7841	0.7818

^a Nominal $\langle S^2 \rangle$ value for a doublet is 0.7500.

5. Computational details

All calculations were performed at the unrestricted DFT level using B3PW91 functional [29,30] with DZ basis set for vanadium [31] and pVDZ basis sets for main group atoms [31]. Molecular structures of all vanadocene(IV) complexes (**1**, **3–11**) were optimized adopting the C_2 symmetry for all complexes. The 3×3 hyperfine interaction tensor A can be separated into isotropic (A_{iso}) and anisotropic (T) components ($A = A_{iso} + T$). First order approximation was used for calculations of HFC tensor, neglecting the spin-orbit coupling and relativistic corrections. This method was successfully used for HFC tensor calculations of 3d transition metal complexes [21,22]. The HFC tensors at the X-ray structures of complexes Cp_2VCl_2 [1], $Cp_2V(OOCCl_3)_2$, $Cp_2V(OOC)_2 \cdot (COOH)_2$ were also calculated. Gaussian 98.7 program [32] was used for DFT calculations.

6. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 214706 and 214707 for **9** and **11**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road Cambridge, CB2 1EZ UK, fax. (int code) +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www:<http://www.ccdc.cam.ac.uk>.

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