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Acetonitrilechlorotris(η^5-cyclopentadienyl)-vanadium(IV) tetrachloroferrate(III)

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The structure of the title compound, $[V(C_5H_5)_2Cl(C_2H_3N)][FeCl_4]$, a potential spermicidally active species, has been determined. This compound has a typical bent metallocene structure, in which two η^5-bonded cyclopentadienyl rings, an N-coordinated acetonitrile molecule and a Cl ligand occupy tetrahedral positions around the V^{IV} atom. The V—N bond length was found to be 2.087 (2) Å.

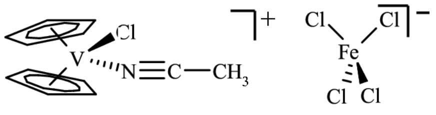
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.022
wR factor = 0.054
Data-to-parameter ratio = 21.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In recent years, vanadocene(IV) complexes have attracted attention because they show biological activity. Neutral vanadocene halide and pseudohalide complexes are largely studied for their antitumour properties (Köpf-Maier & Köpf, 1987), and some cationic vanadocene compounds show significant spermicidal activity (D′Cruz *et al.*, 1998). Recently, the crystal structures of cationic complexes with chelate-bonded acetylacetonate (Ghosh *et al.*, 2001), dithiocarbamate (Ghosh *et al.*, 1998), bipyridine (Ghosh *et al.*, 1999), phenanthroline (Ghosh *et al.*, 1999), *etc.*, have been reported. In this paper, we report the preparation and crystal structure of the title cationic vanadocene complex, (I), with a coordinated acetonitrile.


(I)

Compound (I) (Fig. 1) is the product of the reaction of vanadocene dichloride (Cp_2VCl_2) with acetonitrile in the presence of a Lewis acid ($FeCl_3$). The typical bent metallocene structure was found for (I), in which two η^5-bonded cyclopentadienyl rings, an N-bonded acetonitrile and a Cl ligand occupy the pseudotetrahedral coordination sites around the vanadium(IV) atom [$Cg1—V—Cg2$ 134.10 (4)° and Cl—V—N 85.17 (4)°; $Cg1$ and $Cg2$ are the centroids of the rings C1–C5 and C6–C10, respectively]. The cyclopentadienyl rings have an eclipsed conformation, with $Cg1—V$ and $Cg2—V$ bond lengths of 1.956 (1) and 1.958 (1) Å, respectively. The V—N bond distance [2.087 (2) Å] is comparable with that observed in the methyl derivative $[Cp_2VMe(NCCH_3)][B(C_6H_5)_4]$ [2.096 (4) Å; Choukroun *et al.*, 2002], and lies between the corresponding values for compounds with a bonded heterocycle, $[Cp_2V(bpy)][OTf]_2$ [2.128 (2) and 2.129 (2) Å; Ghosh *et al.*, 1999] and $[Cp_2V(phen)][OTf]_2$ [2.1344 (18) and 2.1386 (19) Å; Ghosh *et al.*, 1999], and for pseudohalide complexes $[Cp_2V(NCS)_2$ and $(C_5H_4CH_3)_2V(NCO)_2]$, where

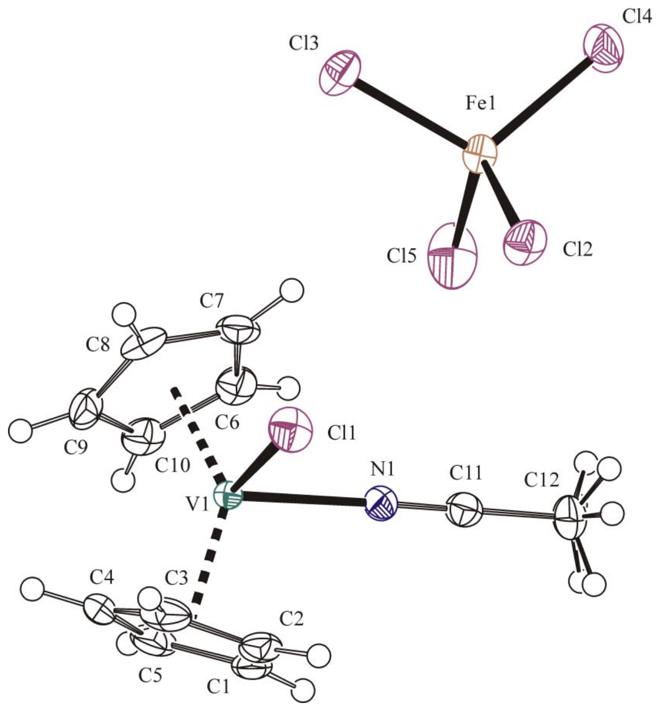


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

V—N bond lengths range from 2.034 (2) to 2.0381 (15) Å (Honzíček *et al.*, 2004, 2005).

Experimental

The title compound was prepared by reaction of vanadocene dichloride (Cp_2VCl_2) with acetonitrile in the presence of $FeCl_3$ as a Lewis acid. Cp_2VCl_2 (0.5 g, 2.0 mmol) was partially dissolved in acetonitrile (20 ml). To this solution, $FeCl_3$ (0.33 g, 2.0 mmol) was added. The rest of the Cp_2VCl_2 dissolved immediately and the colour of the solution changed to dark green. The volatiles were removed *in vacuo* and the concentrated solution was then filtered at 313 K. After cooling of the filtrate to 263 K, dark green crystals of (I) were obtained. These were washed with ether and dried *in vacuo* (0.82 g, yield 91%). Crystals of (I) suitable for X-ray structure analysis were prepared by slow cooling of an acetonitrile solution of (I) at 263 K. The IR and Raman spectra of (I) exhibit a number of characteristic bands originating from the fundamental vibrations of the bis(cyclopentadienyl)vanadium moiety (in cm^{-1}): C—H stretching [IR 3119 (*s*), Raman 3098 (*m*)], C—C stretching [IR 1447 (*vs*), 1433 (*vs*)], Cp-ring breathing [IR 1129 (*w*), Raman 1129 (*vs*)] and C—H bending [IR 1032 (*s*), 1012 (*s*, in the plane of the Cp ring), 856 (*vs*), 842 (*vs*, out of the plane of the Cp ring)] (Diana *et al.*, 1997). The presence of a bonded acetonitrile was inferred from intense bands of $C\equiv N$ stretching [IR 2319 (*s*), 2291 (*s*)] and C—H stretching [IR 2924 (*m*), Raman 2924 (*s*)]. Positive-ion MS (ESI): *m*/*z* 216 $[Cp_2VCl]^+$ (100%). Positive-ion MS/MS of 216: *m*/*z* 198 $[Cp_2V{+}OH]^+$, 181 $[Cp_2V]^+$ (100%), 169 $[CpVCl{+}H_2O]^+$, 151 $[CpVCl]^+$, 133 $[CpV{+}OH]^+$, 81. Negative-ion MS: *m*/*z* 198 $[FeCl_4]^-$ (100%), 161 $[FeCl_3]^-$. Negative-ion MS/MS of 198: *m*/*z* 161 $[FeCl_3]^-$ (100%).

Crystal data

$[V(C_5H_5)_2Cl(C_2H_3N)][FeCl_4]$
$M_r = 455.27$
Orthorhombic, $P2_12_12_1$
$a = 7.3730$ (2) Å
$b = 13.5290$ (3) Å
$c = 17.2680$ (3) Å
$V = 1722.47$ (7) Å^3
$Z = 4$
$D_x = 1.756$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 27 318 reflections
$\theta = 1$–27.5°
$\mu = 2.15$ mm^{-1}
$T = 150$ (2) K
Plate, green
0.5 × 0.42 × 0.18 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: integration (Gaussian; Coppens & Hamilton, 1970)
$T_{min} = 0.405$, $T_{max} = 0.712$
26 509 measured reflections

3946 independent reflections
3789 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.054$
$S = 1.05$
3946 reflections
185 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 0.6271P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Absolute structure: Flack (1983), 1677 Friedel pairs
Flack parameter: −0.003 (13)

Table 2
Selected geometric parameters (Å, °).

*Cg*1—V1	1.956 (1)	V1—Cl1	2.3685 (6)
Cg2—V1	1.958 (1)	N1—C11	1.138 (3)
V1—N1	2.0873 (16)	C11—C12	1.451 (3)
*Cg*1—V1—*Cg*2	134.10 (4)	C11—N1—V1	178.70 (17)
N1—V1—Cl1	85.17 (5)		

Notes: Cg1 is the centroid of atoms C1—C5 and Cg2 is the centroid of atoms C6—C10

The positions of all H atoms were found in a difference Fourier map, including six positions for the disordered CH_3 group. All H atoms were then placed in ideal positions and were refined as riding on their respective parent atom, with C—H distances in the range 0.93–0.96 Å. $U_{iso}(H) = 1.2U_{eq}(C)$ for the cyclopentadienyls. For the first trio of H atoms of the disordered CH_3 group of MeCN, the $U_{iso}(H)$ values were refined, while for the second trio they were set to $1.5U_{eq}(C)$.

Data collection: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *COLLECT* and *DENZO*; data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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