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Crystallographic report

Bis(η^5-methyl-cyclopentadienyl)-bis(cyanato)-vanadium(IV)

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The crystal structure of the first cyclopentadienyl vanadium(IV) pseudohalide complex, (η^5-$C_5H_4CH_3)_2V(NCO)_2$, was determined. The molecule has a typical bent metallocene structure in which two η^5-bonded methyl-cyclopentadienyl rings and two nitrogen atoms of cyanato ligands occupy the pseudotetrahedral coordination sites around the vanadium(IV) center. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: methyl-cyclopentadienyl; vanadocene; pseudohalide; crystal structure

COMMENT

With the exception of the parent compound (η^5-$C_5H_5)_2VCl_2$[1] and several ring-substituted[1–3] and *ansa*-bridged[4–6] vanadocene dichlorides that have been studied by single-crystal X-ray diffraction methods, no other halide or pseudohalide analogues of vanadocene(IV) have so far been structurally determined. The title compound, (η^5-$C_5H_4CH_3)_2V(NCO)_2$, has a distorted tetrahedral geometry (Fig. 1). The vanadium–ring centroid distances (1.973(1) and 1.981(1) Å) are slightly shorter than those in (η^5-$C_5H_4CH_3)_2VCl_2$ (1.99 Å)[2] and longer than in vanadocene(IV) compounds with unsubstituted cyclopentadienyl rings (1.96 Å).[1,7–9] The V–N distances (2.03 Å) are shorter than in [(η^5-$C_5H_5)_2V(bpy)][OTf]_2$ (2.14 Å)[10] and [(η^5-$C_5H_5)_2V(phen)][OTf]_2$ (2.13 Å).[10] The cyclopentadienyl rings have a staggered conformation, with one methyl group located above the $V(NCO)_2$ group with the second one at the side. The significant deviation of angles V–N–C from 180° (V(1)–N(1)–C(1) = 150.2(2)°, V(1)–N(2)–C(2) = 163.5(2)°) is due to the influence of C–H···O intermolecular hydrogen interactions (Fig. 2), forming a zigzag chain of molecules along the *b*-axis (C(24)···O(1) 3.376(3)Å, C(24)–H(24)···O(1) 166°; C(14)···O(2) 3.189(3) Å, C(14)–H(14)···O(2) 125°).

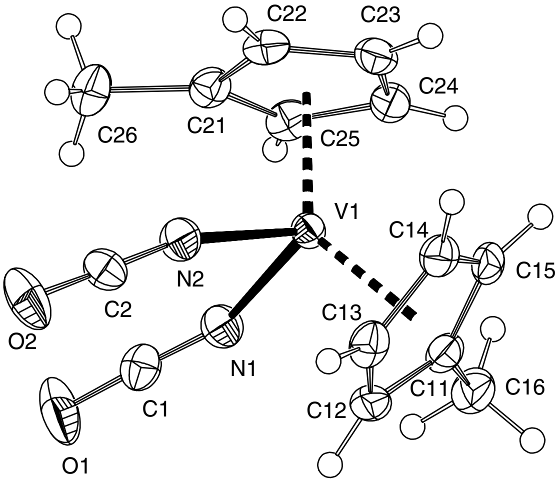

Figure 1. ORTEP drawing of molecular structure of (η^5-$C_5H_4CH_3)_2V(NCO)_2$ (ellipsoids: 50% probability). Important bond distances (Å) and angles (deg): Cp(1)–V(1) 1.973(1), Cp(2)–V 1.981(1), Cp(1)–V(1)–Cp(2) 133.83(4), V(1)–N(1) 2.034(2), V(1)–N(2) 2.036(2), N(1)–V(1)–N(2) 86.62(9), N(1)–C(1) 1.172(3), N(2)–C(2) 1.167(3), C(1)–O(1) 1.200(3), C(2)–O(2) 1.208(3), V(1)–N(1)–C(1) 150.2(2), V(1)–N(2)–C(2) 163.5(2), N(1)–C(1)–O(1) 177.0(3), N(2)–C(2)–O(2) 178.8(3).

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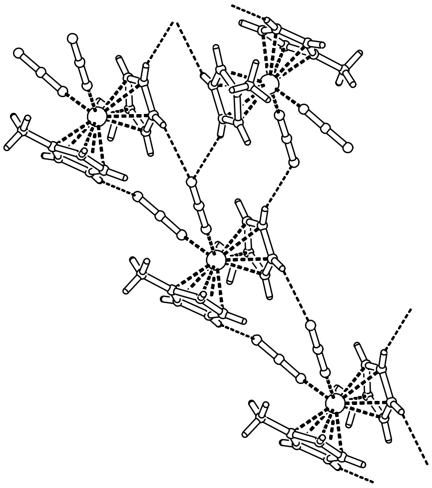

Figure 2. Part of the week C–H···O hydrogen bonds network.

EXPERIMENTAL

Synthesis

(η^5-$C_5H_4CH_3$)$_2$$VCl_2$ (20 mg, 0.071 mmol) was dissolved in freshly distilled, deoxygenated water (5 ml) at room temperature. After complete dissolution, the solution was filtered through a Schlenk frit. The resulting filtrate was mixed with a previously filtered aqueous solution of potassium cyanate (11 mg, 0.142 mmol KOCN in 5 ml water). After the solution was left to stand for 20 min, green crystals suitable for X-ray diffraction analysis were grown.

Crystallography

Crystal data for: $C_{14}H_{14}N_2O_2V$, $M_r = 293.21$, $0.2 \times 0.2 \times 0.1$ mm^3, monoclinic, $C2/c$, $a = 27.3450(13)$ Å, $b = 7.7840(4)$ Å, $c = 13.6530(8)$ Å, $\beta = 119.956(3)°$, $V = 2517.9(2)$ Å^3, $Z = 8$, $D_c = 1.547$ g cm^{-3}. Nonius KappaCCD diffractometer, $T = 150(2)$ K, $\theta_{max} = 27.52°$, μ(Mo Kα) $= 0.786$ mm^{-1}, $\lambda = 0.710\,73$ Å, 16 641 measured reflections, 2879 independent, $R_{int} = 0.063$, 2049 reflections with $I > 2\sigma(I)$, $R = 0.041$ for observed diffractions, $\omega R(F^2) = 0.1036$ for all diffractions. Program used: DENZO-SMN,[11] Sir92,[12] SHELXL97.[13] CCDC number: 225798.

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