APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 71–72
Materials, Nanoscience and Catalysis
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.578

Crystallographic report

The [bis(η^5-methylcyclopentadienyl)titanium(IV)-bis(*N*-methylglycine)] dichloride

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Received 21 July 2003; Accepted 15 October 2003

The crystal network of $[Cp'_2Ti(N{-}CH_3{-}Gly)_2]^{2+}[Cl^-]_2$ ($Cp' = (CH_3)C_5H_4$) complex, which crystallizes as a solvate with CH_3OH, is built up with discrete cationic units connected through intermolecular H···Cl bonds. The α-amino acid ligands are attached through an intramolecular H···O bond within one cationic unit. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; titanium; α-amino acids

COMMENT

The very first example of the crystal structure of a DMTDC–α-amino acid complex is reported (DMTDC = Cp'_2TiCl_2, where $Cp' = \eta^5$-$(CH_3)C_5H_4$). The α-amino acid ligands are coordinated to titanium atom exclusively 'via' the oxygen of the carboxylic group. The coordinated carboxyl group has similar types of C–O bond length as found in esters: O(1)–C(1) 1.2901(19), C(1)–O(2) 1.222(3), O(3)–C(5) 1.293(2), C(5)–O(4) 1.216(2) Å.[1,2] Neighbouring cationic units are attached through H···O and H···Cl bonds within the crystal cell (Fig. 1). A close intramolecular H···O bond between the oxygen of the carboxylic group of one ligand and the ammonium group hydrogen of the second one represents a unique example of such interaction for this class of compounds.[3–5] Only a slight effect on the titanium–ligand bonding angles was observed, regarding exchange of chloride ligands in the cis-position for α-amino acid ligands; Cp′(1)(centroid)–Ti–Cp′(2)(centroid), L–Ti–L (L = Cl or *N*-CH_3–Gly): complex 133.06(4), 95.16(5)°; DMTDC 130.2, 93.15(8)°.[6]

EXPERIMENTAL

The DMTDC (1.000 g, 3.61 mmol), *N*-CH_3–Gly (0.643 g, 7.22 mmol) and distilled water (0.15 ml, 8.33 mmol) were stirred in 10 ml of dry

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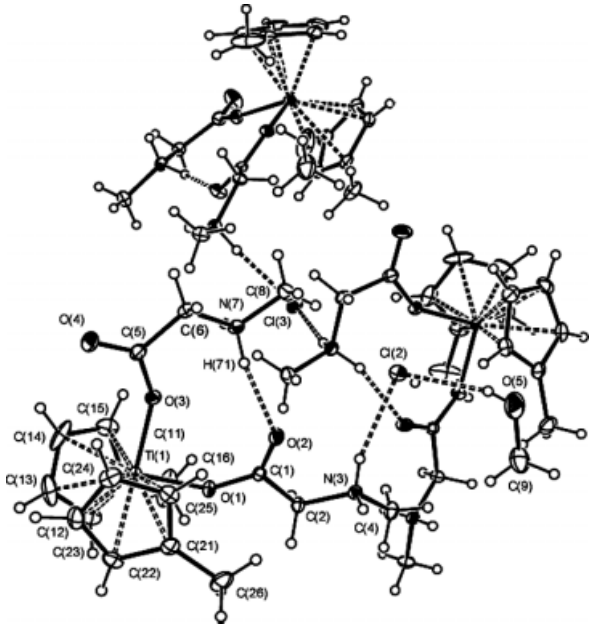

Figure 1. Molecular structure of $[Cp'_2Ti(N\text{-Me}{-}Gly)_2]^{2+}[Cl^-]_2$, cation ··· anion interaction of three cationic units. Key geometric parameters: Ti–Cp′(1)(centroid) 2.0565(10), Ti–Cp′(2)(centroid) 2.0544(9), Ti–O(1) 1.9791(12), Ti–O(3) 1.9430(12), O(1)–C(1) 1.290(2), C(1)–O(2) 1.221(2), O(3)–C(5) 1.293(2), C(5)–O(4) 1.216(2); Cp′(1)(centroid)–Ti–Cp′(2)(centroid) 133.06(4), O(1)–Ti–O(3) 95.16(5), O(1)–C(1)–O(2) 126.79 (15), O(3)–C(5)–O(4) 125.78(17)°; H bonds: H(5)···Cl(2) 2.40(3), H(31)···Cl(3) 2.20 (2), H(72)···Cl(3) 2.20(2), H(71)···O(2) 2.01(2) Å.

methanol at 20 °C under an argon atmosphere (24 h) and mixed with 30 ml of dry Et_2O/CH_2Cl_2 (5 : 1 v/v) for 1 h. Precipitated material was separated, washed with dry CH_2Cl_2 (3 × 5 ml) and dried in vacuum. Crystal preparation: 100 mg of solid was dissolved in a minimal volume of dry methanol, filtered and cooled to 0 °C. Yield: 1.516 g (92.3%), analytically pure product; m.p. >143 °C (dec.), hydroscopic orange solid, solvate with CH_3OH. IR (KBr, cm^{-1}): 3440 vs,b ($\nu_{as}(NH_3)$), 2984w + 2971w + 2931s (B_2, B_1, A_1 $\nu(CH_3)$), 1665 + 1659 vs ($\nu_{as}(COO)$), 1502 vs ($\nu(C–CH_3)$), 1379 m ($\nu_s(COO)$), 1254 + 937 m ($\nu(C–C)$, Cp). ^1H NMR (ppm): 2.09 (s, C_5H_4–CH_3, 6H), 2.76 (s, *N*-CH_3, 6H), 3.19 (CH_3OH), 3.79 (s, α-CH_2, 4H), 6.40 and 6.75 (2 × m, 8H, C_5H_4, in ascending order: $H_2 + H_5$ and $H_3 + H_4$; $J^3(H_2H_3) = 4.84$ Hz, $J^4(H_2H_4) = 2.42$ Hz). ^{13}C NMR (ppm): 18.59 (CH_3), 36.81 (*N*-CH_3), 53.91 (CH_2), 121.28, 125.81, 141.30 (C_5H_4), 174.31 (COO). ^{14}N NMR (ppm): −335.68. Intensity data were collected at 150 K on Nonius Kappa CCD area detector diffractometer for a red block 0.15 × 0.20 × 0.35 mm^3. $C_{18}H_{28}N_2O_4Ti{\cdot}2(Cl){\cdot}CH_4O$, $M = 487.24$, centric, orthorhombic *Pbca* no. 61, $a = 9.5310(3)$, $b = 18.2980(5)$, $c = 26.6350(5)$ Å, $V = 4645.1(2)$ $Å^3$, $Z = 8$, $D_{calc} = 1.3934$ g cm^{-3}, 5307 unique data ($\theta_{max} = 27.5°$), $R = 0.0353$ (all data), $\omega R = 0.08$ (all data). Programs used: SHELXL 97, PLATON for Windows v.1.05, ORTEP III v.1.0.3. CCDC deposition number: 205636.

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