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Crystallographic report

The [bis(η^5-cyclopentadienyl)titanium(IV)-bis(L-methionine)] dichloride

Radim Bína[1]*, Ivana Císařová[2], Martin Pavlišta[1] and Ivan Pavlík[1]

[1]Research Centre "New Inorganic Compounds and Advanced Materials", University of Pardubice, Nam. Cs. Legii 565, 532 10 Pardubice, Czech Republic
[2]Charles University, Faculty of Natural Sciences, Hlavova 2030, Albertov 6, 128 43 Prague, Czech Republic

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The structure of ionic complex $[Cp_2Ti(\text{L-Met})_2]^{2+}[Cl^-]_2$ (where $Cp = \eta^5\text{-}C_5H_5$) possessing C_2 symmetry is presented. Discrete cationic units with distorted tetrahedral geometry around the central titanium atom are connected through intermolecular H···Cl bonds between ammonium group protons of α-amino acid ligands and chloride anions. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: titanocene dichloride; α-amino acids

COMMENT

In a recent study we were involved in the synthesis and structural characterization of model complexes of the antitumour-active titanocene dichloride (TDC) with essential α-amino acids bearing a sulfur atom in their side chain, i.e. Cys, *S*-substituted Cys and Met. Herein, we present the structure of one of these compounds. The molecular structure of the TDC-L-Met complex **1** (Fig. 1) shows that α-amino acid ligands are coordinated to the central titanium atom exclusively through the oxygen of the carboxylic group[1,2] and that no Ti–S interaction is present. Neighbouring cations are connected through intermolecular hydrogen bonds between $NH_3{}^+$-protons of α-amino acid ligands and chloride anions. Carboxyl group structural features and C–O bond lengths and angles compare well with those found in esters.[3] Compared with TDC,[4] shortening of titanocene core bond lengths and Ti–L bond lengths, as well as changes in appropriate bond angles, was observed regarding the exchange of ligands in the cis-position; average bond distances Ti–Cp(c), Ti–L: complex **1** 2.0482, 1.9694 Å; TDC 2.058, 2.364 Å; bond angles Cp1(c)–Ti–Cp2(c), L–Ti–L: complex **1** 132.33, 89.10; TDC 130.89, 94.43° (L = Cl or $\text{L-OOCCHNH}_3\text{CH}_2\text{CH}_2\text{SCH}_3$; Cp(c) = ring centre). During the preparation of suitable monocrystals for X-ray structure determination, we found an interesting behaviour with complex **1**. Only crystals with the LL combination of isomers (*S*,*S* in the absolute configuration) were grown, although complex **1** contains both optical isomers. Most probably, during the slow process of the single crystal growth, prior formation of those having the LL-combination of isomers (possessing C_2 symmetry of crystal units) was perhaps somewhat preferred to other possibilities (DD and/or DL). A similar feature was also reported for TDC-D,L-4-fluorophenylalanine complex,[2] where, on the contrary, the DD-combination of isomers was found to be favoured. Thus, perchance, we have met with a similar situation for complex **1**.

EXPERIMENTAL

The TDC (2.00 g, 8.0 mmol), D,L-methionine (2.40 g, 16.0 mmol) and distilled water (0.30 ml, 16.7 mmol) were stirred in 5 ml of dry methanol at 20 °C under an argon atmosphere. Light-orange solid, precipitated over 30 min, was filtered off, washed with dry CH_2Cl_2 (3 × 5 ml) and dried in vacuum. Suitable crystals were prepared by slow evaporation of solvent from the saturated solution of **1**, while holding the solution at 0 °C. Yield: 1.516 g (96.4%), analytically pure product; m.p. >175 °C (dec), light-orange solid. ^{1}H NMR: 2.18 (m, CH_3, 6H), 2.22 (m, CH_2, 4H) 2.72 (t, SCH_2, 4H), 4.11 (t, CH, 2H) 6.67 (s, Cp, 10H). ^{13}C NMR: 18.08 (CH_3), 32.89 (CH_2), 33.47 (SCH_2), 57.14 (CH), 122.99 (Cp), 177.28 (COO); ^{14}N NMR: −345.48. IR (KBr, cm^{-1}): 3442 vs,b ($\nu_{as}(NH_3)$), 1665 vs (ν_{as}(COO)), 1350 s (ν_s(COO)), 1133 w (ν(C–C),Cp), 827 s-vs (ν(C–H),Cp). Raman: 1667 (ν_{as}(COO)), 1366 (ν_s(COO)), 1132 (9) (ν(C–C),Cp), 826 (ν(C–H),Cp), 261 (a_1-Cp tilting). Intensity data were collected at 150 K on Nonius Kappa CCD area detector diffractometer for a block 0.40 × 0.25 × 0.20 mm^3; colour: orange–red. $C_{20}H_{32}N_2O_4S_2Ti \cdot 2(Cl)$, $M = 547.40$, monoclinic, space group C_2 (no. 5), $a = 29.1170(6)$, $b = 7.82300(10)$, $c = 11.6340(5)$ Å,

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*Correspondence to: Radim Bína, Research Centre "New Inorganic Compounds and Advanced Materials", University of Pardubice, Nam. Cs. Legii 565, 532 10 Pardubice, Czech Republic.
E-mail: bina@lachema.cz

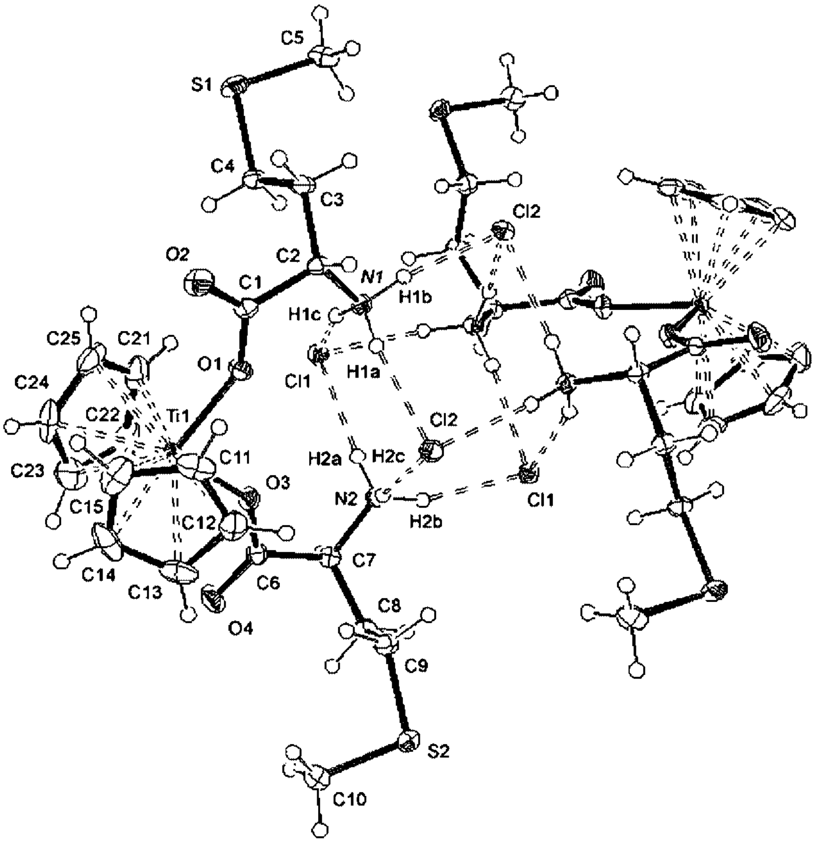

Figure 1. Molecular structure of $[Cp_2Ti(L\text{-}Met)_2]^{2+}[Cl^-]_2$ — cation···anion interaction of two units (ORTEP plot, thermal ellipsoids with 40% probability). Key geometric parameters: Ti–Cp1(c) 2.0480(13) (Cp1 ring slippage: 0.042 Å), Ti–Cp2(c) 2.0484(10) (Cp2 ring slippage: 0.037 Å), Ti–O1 1.9728(13), Ti–O3 1.9660(13), O1–C1 1.292(2), C1–O2 1.211(2), O3–C6 1.289(2), C6–O4 1.218(2) Å; Cp1(c)–Ti–Cp2(c) 132.33(5), O1–Ti–O3 89.10(6), O1–C1–O2 126.06(17), O3–C6–O4 125.85(17)°; H bonds: H1a···Cl2 2.27(3), H1b···Cl2 2.22(3), H1c···Cl1 2.40(3), H2a···Cl1 2.30(2), H2b···Cl1 2.21(2), H2c···Cl2 2.36(2) Å.

$\beta = 106.5580(11)°$, $V = 2540.13(8)$ Å^3, $Z = 4$, $D_{calc} = 1.431$ g cm^{-3}, 5766 unique data ($\theta_{max} = 27.47°$), $R = 0.033$ (all data), $\omega R = 0.0586$ (all data), $\rho_{max} = 0.209$ e$^-$ Å^{-3}. Programs used: audit creation method-SHELXL 97; PLATON for Windows v.1.05;[5] ORTEP III for Windows.[6] CCDC deposition number 220526.

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