Reaction of Titanocene Dihalides with Na$_2$H$_2$EDTA. Crystal Structure of [Ti(EDTA)(H$_2$O)]

N. Klouras$^{1,*}$, N. Tzavellas$^1$, and C. P. Raptopoulou$^{2,*}$

$^1$ Department of Chemistry, University of Patras, GR-26500 Patras, Greece
$^2$ Institute of Materials Science, NRCPS "Demokritos", GR-15310 Athens, Greece

Summary. Titanocene complexes ([Ti($\eta^5$-C$_5$H$_5$R)$_2$X$_2$]; R : H, SiMe$_3$; X : Cl, Br) react with Na$_2$H$_2$EDTA in aqueous methanol to give an identical product (Ti(EDTA)(H$_2$O)) by cleavage of the halogen and cyclopentadienyl ligands. The structure of [Ti(EDTA)(H$_2$O)] has been determined by X-ray diffraction; crystal data: monoclinic $a = 13.923(6)$, $b = 7.048(3)$, $c = 13.252(5)$ Å, $\beta = 90.81(1)^\circ$, space group $P2_1/c$, $Z = 4$. In this complex, Ti has a sevenfold coordination with a hexadentate EDTA$^{4-}$ ligand and a water molecule occupying an additional coordination site.

Keywords. Titanium; EDTA; Crystal structure; Sevenfold coordination.

Introduction

Numerous reactions of titanocene dichloride with various bidentate chelating ligands (acetylacetone [1], 1,2-benzenedithiol [2], $\alpha$-aminothiophenol [3], pentasulfide or pentaselenide dianion [4], etc.) have been published. In all resulting compounds the titanium atom is four-coordinate. In contrast, the six-coordinate complex [Ti($\eta^5$-C$_5$H$_5$)Cl$_2$] has been obtained by action of 8-hydroxyquinoline ($\alpha$H) on [Ti($\eta^5$-C$_5$H$_5$)Cl$_2$] [5]. To our knowledge, no reactions of titanocene dihalides with the hexadentate ethylenediaminetetraacetate ion (EDTA)$^{4-}$ have been reported. This excellent chelating ligand has long been known and studied as calcium binding agent, not only with respect to practical applications but also as classic research model for polydentate chelation. In the usual case of hexadentate
chelation by \((EDTA)^{4-}\), the coordination number of the metal ion in the complexed species becomes \(6, 7, 8, 9, \ldots\) as \(0, 1, 2, 3, \ldots\) water molecules are retained in the coordination sphere. Since ring constraints are incompatible with a quasi-octahedral configuration except for a central cation of relatively small size, coordination numbers greater than six are expected for larger central cations. In fact, previous X-ray structural studies of aquo complexes such as \([\text{Mn}(EDTA)(H_2O)]^2-\) \([6]\), \([\text{Ca}(EDTA)] \cdot 7H_2O\) \([7]\), \([\text{La}(EDTA)(H_2O)_3]^2-\) \([8]\), and \([\text{La}(EDTA)(H_2O)_4]\) \([9]\) have revealed coordination numbers of \(7, 8, 9,\) and \(10,\) respectively. In the present work we describe the synthesis and structure of the seven-coordinate \([\text{Ti}(EDTA)(H_2O)]\) complex.

**Results and Discussion**

The reaction between titanocene dihalogenides and \(\text{Na}_2H_2EDTA\) may be represented by the equation

\[
[Ti(\eta^5-C_5H_4R)_2X_2] + H_2EDTA^{2-} + H_2O \rightarrow [Ti(EDTA)(H_2O)] + 2C_5H_5R$
\[+ 2X^- (R = H, SiMe_3; X = Cl, Br)\]

An analogous cleavage of the cyclopentadienyl-titanium also occurs, even under rigorous conditions, when solutions of \([M(\eta^5-C_5H_2)_2X_2] (M = Ti, Zr, Hf; X = Cl, Br)\) are refluxed with the bidentate chelating agent 8-hydroxy-quinoline \([5]\).

The air-stable \([Ti(EDTA)(H_2O)]\) is sparingly soluble in benzene and tetrahydrofuran and moderately soluble in \(\text{CHCl}_3,\) acetone, and methanol to give orange-yellow solutions.

**Crystal structure of \([Ti(EDTA)(H_2O)]\)**

The molecular structure of \([Ti(EDTA)(H_2O)]\) is shown in Fig. 1. For the titanium atom, the coordination number is 7, and the coordination polyhedron is approximately pentagonal bipyramidal. One site, in addition to the six occupied by the hexadentate \(EDTA\) ligand, is filled by a water molecule (\(OW\)). The hexadentate chelation of \(EDTA\) gives rise to five-membered rings, the ethylenediamine ring and

![Fig. 1](image-url)