Monatshefte für Chemie 128, 1201–1206 (1997)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Reaction of Titanocene Dihalides with Na_2H_2EDTA. Crystal Structure of [Ti(*EDTA*)(H_2O)]

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Summary. Titanocene complexes ([Ti(η^5-$C_5H_4R)_2X_2$]; R = H, $SiMe_3$; X = Cl, Br) react with Na_2H_2EDTA in aqueous methanol to give an identical product ([Ti(*EDTA*)(H_2O)] by cleavage of the halogen and cyclopentadienyl ligands. The structure of [Ti(*EDTA*)(H_2O)] has been determined by X-ray diffraction; crystal data: monoclinic $a = 13.923(6)$, $b = 7.048(3)$, $c = 13.252(5)$ Å, $\beta = 90.81(1)°$, 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.

Reaktion von Titanocen-Dihalogeniden mit Na_2H_2EDTA. Kristallstruktur von [Ti(*EDTA*)(H_2O)]

Zusammenfassung. Titanocenkomplexe ([Ti(η^5-$C_5H_4R)_2X_2$]; R = H, $SiMe_3$; X = Cl, Br) reagieren in wäßrigem Methanol mit Na_2H_2EDTA unter Verdrängung der Halogen- und Cyclopentadienyl-liganden zum selben Produkt ([Ti(*EDTA*)(H_2O)]). Die Struktur von ([Ti(*EDTA*)(H_2O)]) wurde röntgenographisch bestimmt. Kristalldaten: monoklin, $a = 13.923(6)$, $b = 7.048(3)$, $c = 13.252(5)$ Å, $\beta = 90.81(1)°$, Raumgruppe $P2_1/c$, $Z = 4$. In diesem Komplex ist das Titanatom mit einem sechszähnigen *EDTA*-Liganden und einem Wassermolekül, das eine zusätzliche Koordinationsstelle besetzt, siebenfach koordiniert.

Introduction

Numerous reactions of titanocene dichloride with various bidentate chelating ligands (acetylacetone [1], 1,2-benzenedithiol [2], *o*-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(η^5-C_5H_5)Cl*ox*$_2$] has been obtained by action of 8-hydroxyquinoline (*ox*H) on [Ti(η^5-C_5H_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, ... as 0, 1, 2, 3, ... 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 $[Mn(EDTA)(H_2O)]^{2-}$ [6], $Ca[Ca(EDTA)]\cdot 7H_2O$ [7], $[La(EDTA)(H_2O)_3]^-$ [8], and $[La(EDTA)(H_2O)_4]$ [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 $[Ti(EDTA)(H_2O)]$ complex.

Results and Discussion

The reaction between titanocene dihalogenides and Na_2H_2EDTA may be represented by the equation

$$[Ti(\eta^5\text{-}C^5H_4R)_2X_2] + H_2EDTA^{2-} + H_2O \rightarrow [Ti(EDTA)(H_2O)] + 2C_5H_5R + 2X^- (R = H, SiMe_3; X = Cl, Br)$$

An analogous cleavage of the cyclopentadienyl-titanium also occurs, even under rigorous conditions, when solutions of $[M(\eta^5\text{-}C_5H_2)_2X_2]$ (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 $CHCl_3$, acetone, and methanol to give orange-yellow solutions.

Crystal structure of [Ti(EDTA)(H$_2$O)]

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

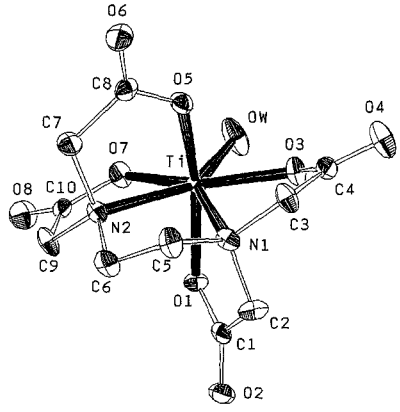

Fig. 1

Table 1. Summary of X-ray data

Empirical formula	$C_{10}H_{14}N_2O_9Ti$
Formula weight	354.13
Temperatute, K	298
Wavelength	MoK_α, 0.71073 nm
Space group	$P2_1/c$
a (Å)	13.923(6)
b (Å)	7.048(3)
c (Å)	13.252(5)
β (deg)	90.88(1)
V ($Å_3$)	1300.4(9)
Z	4
$D_{calcd}D_{measd}$ ($g \cdot cm^{-3}$)	1.809 / 1.78
Abs. coeff. (μ, mm^{-1})	0.712
Scan mode / speed (deg / min)	θ-2θ / 4.0
Scan range (deg)	2.5 $+\alpha_1\alpha_2$ separation
θ range (deg)	1.46 to 27.00
Reflections collected	2940
Independent reflections	2814 (R[int = 0.0086)
Range of h, k, l	$-17 \rightarrow 17$, $0 \rightarrow 9$, $0 \rightarrow 16$
F(000)	728
$[\Delta/\sigma]_{max}$	0.010
W^a	$a = 0.0115\, b = 0.8680$
$(\Delta_\rho)_{max}/(\Delta_\rho)_{min}$ ($e/Å^3$)	0.299 and −0.268
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2814 / 0 / 256
Goodness-of-fit on F^2	1.091
R indices (3846 refs $I > 2\sigma(I)$)^b	$R_1 = 0.0286$, $wR_2 = 0.0776$
R indices (all data)	$R_1 = 0.0300$, $wR_2 = 0.0787$

[a] $W = 1/(\sigma^2(F_o^2) + (a^*P + b^*P)$ and $P = (\text{Max}\ (F_o^2, 0) + 2^*Fc^2)/3$ [b] R_1 based on Fs, wR_2 based on F^2 extinction coefficient 0.070(4)

four glycinate rings; consequently, the conformation of these rings can be used to describe the geometry of the *EDTA* ligand in the complex. The glycinate rings are fused either equatorially (*G eq* rings) or axially (*G ax* rings) to a central ethylenediamine ring (*E* ring), and the titanium atom is common to each ring. The structural parameters of these rings characterizing the geometry of the *EDTA* ligand are given in Table 3.

All chelate rings in *EDTA* complexes investigated so far are significantly ruffled [10]. A gross measure of the ruffling in a five-membered glycinate ring is provided by the deviation of the sum of the interior angles from 540° which corresponds to planarity. Values for this sum in the [Ti(*EDTA*)(H_2O)] complex range from 515.3° (*E* ring) to 534.6° (G_1 ring). It should be noted that the sum of the interior angles in an axial glycinate ring (mean value 534.1°) exceeds that in an equatorial glycinate ring (mean value 526.9°) by 7.2°. Thus, axial rings are less sharply folded and carry

Table 2. Positional ($\times 10^4$) and equivalent thermal parameters ($\times 10^3$) of the non-H atoms; E.s.d.s in parentheses; $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$

Atom	x	y	z	U_{eq}
Ti	250(1)	529(1)	5370(1)	18(1)
OW	2479(1)	−1589(2)	4271(1)	41(1)
O(1)	2176(1)	2759(2)	4601(1)	24(1)
O(3)	1221(1)	−700(2)	5363(1)	27(1)
O(5)	2831(1)	−909(2)	6564(1)	27(1)
O(7)	3750(1)	575(2)	4659(1)	28(1)
O(2)	1314(1)	5357(2)	4283(1)	32(1)
O(4)	8(1)	−1854(2)	6255(1)	42(1)
O(6)	3682(1)	−1379(2)	7988(1)	39(1)
O(8)	4995(1)	2223(2)	4088(1)	36(1)
N(1)	1521(1)	2231(2)	6437(1)	22(1)
N(2)	3496(1)	2560(2)	6249(1)	22(1)
C(1)	1508(1)	4000(2)	4819(1)	23(1)
C(2)	982(1)	3593(3)	5782(1)	28(1)
C(3)	846(1)	854(3)	6888(1)	29(1)
C(4)	640(1)	−696(2)	6134(1)	25(1)
C(5)	2087(1)	3220(3)	7245(1)	28(1)
C(6)	2962(1)	4086(2)	6778(1)	28(1)
C(7)	4046(1)	1336(3)	6974(1)	29(1)
C(8)	3496(1)	−447(2)	7236(1)	26(1)
C(9)	4173(1)	3412(3)	5520(1)	27(1)
C(10)	4357(1)	1998(2)	4688(1)	24(1)

less angular strain than equatorial rings. This strain is particularly apparent in the O–Ti–N and C–O–Ti bond angles within the glycinate rings and, of course, in the N–Ti–N angle of the ethylenediamine ring.

The structural nonequivalence of the two sets of glycinate rings if reflected in the differences of *ca.* 0.06 Å between the Ti–O distances; by contrast, the Ti–N, O–C, C–C, and N–C bond distances are seen to be virtually independent of the ring size. The averaged values of these nearly invariant bond lengths (Ti–N = 2.306, C–C = 1.509, C–N = 1.489, and C–O = 1.313 Å) are typical of those found in other *EDTA* complexes [7, 11, 12]. The mean Ti-N bond length (2.306 Å) is also quite normal [13].

The C–O bond lengths within the carboxylate groups vary as the oxygen atoms O_c and O_u, are or are not coordinated to the metal atom; the averaged distances (C–O_c = 1.313, C–O_u (partial bond character) = 1.214 Å) in this complex correspond to strong Ti-O_c interaction.

Finally, the Ti–OW bond distance (2.086 Å) is significantly longer than that of each Ti–O bond involving a carboxylate oxygen; this is a quite expected result, ascribable to the dominant ionic contribution from the charged glycinate oxygen atom.

Table 3. Selected bond lengths (Å) and angles (°) in [Ti(*EDTA*)(H_2O)]

	Glycinate rings[a]			
	G_1 *ax*	G_2 *eq*	G_3 *eq*	G_4 *ax*
		Distances		
Ti–O[b]	1.9235(13)	1.9816(13)	1.9907(14)	1.9283(13)
Ti–N	2.3155(14)	2.3155(14)	2.2962(14)	2.2962(14)
O–C[c]	1.313(2)	1.313(2)	1.311(2)	1.316(2)
C–C	1.509(2)	1.506(2)	1.511(2)	1.514(2)
N–C	1.490(2)	1.483(2)	1.486(2)	1.493(2)
		Angles		
O–Ti–N	76.36(5)	71.99(5)	72.87(5)	77.17(5)
C–O–Ti	126.16(10)	124.07(10)	124.42(10)	125.52(11)
C–N–Ti	105.92(9)	106.90(10)	107.83(10)	105.37(10)
O–C–C	114.47(14)	113.89(14)	114.20(14)	113.75(14)
N–C–C	111.65(13)	108.82(13)	108.88(13)	111.82(13)
		Torsion angles		
Ti–N–C–C	−23.82	−32.05	−30.92	−26.34
N–C–C–O	17.53	12.48	14.11	21.53
C–C–O–Ti	1.33	20.55	15.41	−2.67
C–O–Ti–N	−12.15	−30.44	−26.00	−10.19
O–Ti–N–C	19.07	32.20	29.56	19.60

		Ethylenediamine ring			
Distances		Angles		Torsion angles	
Ti–N1	2.3155(14)	N1–Ti–N2	73.97(5)	Ti–N1—C5-C6	42.73
Ti–N2	2.2962(14)	Ti–N1–C5	111.78(10)	N1–C5–C6–N2	−55.29
N1–C5	1.492(2)	Ti–N2–C6	112.81(10)	C5–C6–N2–Ti	41.87
N2–C6	1.489(2)	N1–C5–C6	108.41(13)	C6–N2–Ti–N1	−14.45
C5–C6	1.506(2)	N2–C6–C5	108.30(14)	N2–Ti–N1–C5	−15.48

[a] G_1, G_2, G_3, and G_4 denote the glycinate rings beginning with C1, C3, C9, and C7, respectively (Fig. 1); [b] the Ti–O*W* bond distance to the water molecule is 2.086(2) Å; [c] The four C-O distances of the carboxylate oxygen atoms (O2, O4, O6, and O8) that are not complexed to the titanium atom range from 1.213(2) to 1.219(2) Å

Experimental

$[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$, $Na_2H_2EDTA{\cdot}2H_2O$, and methanol (not dried) were obtained from Merck and used as supplied. $[Ti(\eta^5\text{-}C_5H_5)_2Br_2]$ [14] and $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ [15] were prepared by literature methods.

Preparation of [Ti(EDTA)(H_2O)] (General procedure)

4.0 mmol of $[Ti(\eta^5\text{-}C_5H_4R)_2X_2]$ (R = H, $SiMe_3$; X = Cl, Br) and 1.5 g (4.0 mmol) of $Na_2H_2EDTA{\cdot}2H_2O$ were stirred in 10 ml aqueous methanol for 24 h at room temperature. The yellow reaction mixture was evaporated to dryness under vacuum and redissolved in 100 ml of warm methanol. After filtering the solution, the filtrate obtained was cooled at −20°C for two days. The orange-yellow crystalline precipitate formed was filtered off, washed repeatedly with cold methanol, and dried.

Yield: 25–30%; $C_{10}H_{14}N_2O_9Ti$; calc.: C 33.91, H 3.98, N 7.90; found: C 34.22, H 4.13, N 7.74; m.p.: 255°C (dec).

Crystallographic section

Slow crystallization from water at room temperature yielded yellowish prismatic crystals after two weeks. A crystal with approximate dimensions of $0.30 \times 0.35 \times 0.45$ mm was mounted in air. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range of $11 < 2\theta < 23$; they are given in Table 1 together with other data. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. *Lorentz* polarization correction was applied using Crystal Logic software.

The structure was solved by direct methods using the SHELXS-86 program [16] and refined by full-matrix least-squares techniques of F^2 with SHELXL-93 [17]. All hydrogen atoms were located by difference maps and refined isotropically. All non-hydrogen atoms were refined anisotropically.

The positional parameters and the equivalent isotropic temperature factors for the non-hydrogen atoms are collected in Table 2. Hydrogen atomic coordinates and a list of structure factors can be obtained from the authors. A selection of bond distances and angles is given in Table 3.

Acknowledgements

C.P. Raptopoulou thanks Mrs *Athina Athanassiou* for financial support.

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Received March 3, 1997. Accepted June 16, 1997