

**DICYCLOPENTADIENYL TITANIUM(IV) PYRIDINE-2,6-DICARBOXYLATE
COMPLEXES. SYNTHESIS AND STRUCTURAL CHARACTERIZATION
AS PENTACOORDINATE TITANOCENE DERIVATIVES**

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Summary

Reaction of $(C_5H_5)_2Ti(CH_3)_2$ or $(CH_3)_4C_2(C_5H_4)_2Ti(CH_3)_2$ with pyridine-2,6-dicarboxylic acid (dipicolinic acid) yields titanocene dipicolinate derivatives. The molecular structure of $(C_5H_5)_2Ti$ dipicolinate is that of an axially symmetric, pentacoordinate titanocene derivative with two carboxyl oxygen atoms and the pyridine nitrogen atom as ligating atoms. Two identical chelate bite angles of only 71° make the dipicolinate ligand particularly suited to form a remarkably stable titanocene derivative with unprecedented pentacoordinate geometry.

Introduction

The molecular structures of a vast number of dicyclopentadienyltitanium(IV) compounds studied to date have invariably revealed a tetracoordinate, pseudotetrahedral coordination geometry **. These species thus have a 16-valence electron configuration with an unoccupied coordination site available, e.g., for associative reaction steps. Stable pentacoordinate species similar to those well known for other Group IV to VI transition metals [6–11], however, have not previously been observed in any structurally characterized titanocene derivative ***.

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** Cf. ref. 1 and references therein. At the titanium-(II) and -(III) levels, titanocene derivatives with tricoordinate geometry have been reported in a few instances [2–5].

*** Whether complexes with η^2 -coordinated ligands, such as $(C_5H_5)_2Ti(CO)C_2(C_6H_5)_2$ [12] or $(C_5H_5)_2Ti(Cl)OCCH_3$ [13] should be considered as examples of pseudotetrahedral geometry or as exceptions to this rule is debatable. In a number of instances, pentacoordinate or hexacoordinate dicyclopentadienyltitanium(IV) species have been proposed without support from crystal structure determinations [14–19].

In this communication, we report on the synthesis and structural characterization of pentacoordinate titanocene derivatives containing the dipicolinate (pyridine-2,6-dicarboxylate, denoted by dipic) ligand.

Results and discussion

Reaction of dimethyltitanocene, $(C_5H_5)_2Ti(CH_3)_2$, with dipicolinic acid in tetrahydrofuran leads, after evaporation of solvent and subsequent recrystallization from toluene/hexane, in about 60% theoretical yield, to a yellow, microcrystalline material with elemental composition and 1H NMR spectrum (see Table 1) in accord with a complex of composition $(C_5H_5)_2Ti(dipic)$. The material is readily soluble in methylene dichloride, diethyl ether, or toluene*. Slow evaporation from chloroform solution gave crystals suitable for an X-ray crystal structure determination.

Analogous results were obtained when the tetramethylethylene-bridged dimethyltitanocene derivative, $(CH_3)_4C_2(C_5H_4)_2Ti(CH_3)_2$, was treated with dipicolinic acid in tetrahydrofuran. The 1H NMR spectrum of the product showed the signals from the cyclopentadienyl protons as two pseudotriplets, indicating a structure which is axially symmetric on the 1H NMR time scale (Table 1).

For a structural characterization of $(C_5H_5)_2Ti(dipic)$, space group, cell parameters and X-ray diffraction intensities were determined on a Syntex-P3 four-circle diffractometer at 243 K, using $Mo-K_\alpha$ radiation (λ 0.71069 Å), graphite monochromator, ω -scan with $1.8 < \dot{\omega} < 24.3^\circ \text{ min}^{-1}$, $\Delta\omega$ 1.2° and $2 \leq 2\theta \leq 46^\circ$. The space group was found to be $P4_32_12$, with 4 crystallographically equivalent molecules per unit cell. Cell parameters: $a = b = 775.7(4)$, $c = 2239(2)$ pm; $\alpha = \beta = \gamma = 90^\circ$; V $1348 \times 10^6 \text{ pm}^3$; d_{calcd} 1.69 g/cm³; absorption coefficient μ 6.9 cm⁻¹. For solution and refinement of the structure, 867 independent reflexes with $I \geq 2\sigma(I)$ were used; empirical absorption corrections were applied.

TABLE 1

1H NMR SPECTRA OF $(C_5H_5)_2Ti(dipic)$ AND $(CH_3)_4C_2(C_5H_4)_2Ti(dipic)$ IN $CDCl_3$ SOLUTION AT 250 MHz (1H NMR shifts in ppm relative to TMS)

$(C_5H_5)_2Ti(dipic)$		$(CH_3)_4C_2(C_5H_4)_2Ti(dipic)$		Assignment
Shift	Intensity	Shift	Intensity	
6.22	10 (s)	1.61	12 (s)	$(CH_3)_4C_2$
		5.77	4 (t, 2.6 Hz)	C_5H_5
		6.22	4 (6, 2.6 Hz)	C_5H_4
8.28	3 (m) ^a	8.26	3 (m) ^a	NC_5H_3

^a The signals of the pyridine H atoms are only partly resolved and have the appearance of a broadened singlet.

* Other methods commonly employed for the synthesis of titanocene dicarboxylate complexes, such as reaction of $(C_5H_5)_2TiCl_2$ with free carboxylic acid in the presence of triethylamine, or with two equivalents of sodium carboxylate, e.g. in ethanol solution (cf. ref. 1 and literature cited there), in the case of dipicolinic acid or its disodium salt gave mainly products insoluble in $CHCl_3$ or THF (which were probably polymeric species and could not be characterized) and only small quantities of $(C_5H_5)_2Ti(dipic)$.

TABLE 2

STRUCTURAL PARAMETERS FOR $(C_5H_5)_2Ti$ DIPICOLINATE FRACTIONAL COORDINATES (with e.d.s.'s and isotropic thermal parameters)

Atom	x	y	z	U
Ti	0.2632(2)	0.7369(2)	0.25000	
N	0.4601(8)	0.5399(8)	0.25000	
C(1)	0.081(1)	0.527(1)	0.2950(4)	0.037(2)
C(2)	0.046(1)	0.527(1)	0.2343(4)	0.038(3)
C(3)	-0.023(1)	0.692(1)	0.2192(4)	0.034(2)
C(4)	-0.032(1)	0.785(1)	0.2728(4)	0.035(2)
C(5)	0.033(1)	0.687(1)	0.3169(4)	0.036(2)
C(6)	0.545(1)	0.509(1)	0.2995(4)	0.022(2)
C(7)	0.677(1)	0.384(1)	0.3015(4)	0.030(2)
C(8)	0.708(1)	0.292(1)	0.250000	0.032(3)
C(9)	0.493(1)	0.616(1)	0.3502(4)	0.022(2)
O(1)	0.3631(7)	0.7123(8)	0.3373(3)	
O(2)	0.5668(8)	0.6119(8)	0.3976(3)	

TABLE 3

BOND LENGTHS (pm) AND BOND ANGLES ($^\circ$) AT THE Ti ATOM IN $(C_5H_5)_2Ti$ DIPICOLINATE (CR = centroid of C_5 ring; PL = mean plane of C_5 ring)

Ti-O	211.1(6)	O-Ti-N	71.1(2)
Ti-N	216.0(8)	CR-Ti-CR'	133.0
Ti-CR	205.2	PL-PL'	47.2
Ti-PL	205.2		
Ti-C(1)	238(1)		
Ti-C(2)	237(1)		
Ti-C(3)	235(1)		
Ti-C(4)	238(1)		
Ti-C(5)	236(1)		

The structures were solved by direct methods (SHELXTL) and refined with a partially anisotropic model, using a weighting scheme based on counting statistics. Hydrogen atom positions were taken from the Fourier difference map, but not refined. The refinement converged at $R_1 = 0.0773$ and $R_2 = 0.084$, where $R_1 = (\sum \|F_o\| - |F_c|) / \sum |F_o|$ and $R_2 = [\sum \omega (|F_o| - |F_c|)^2]^{1/2} / [\sum \omega |F_o|^2]^{1/2}$. Relevant bond lengths and bond angles are listed in Table 3*.

The molecular structure of $(C_5H_5)_2Ti(dipic)$ (see Fig. 1) is that of an axially symmetric, pentacoordinate metallocene derivative; the Ti atom and the pyridine atoms N and C(8) are located on a crystallographic C_2 axis. The cyclopentadienyl centroids are at a distance of 205.2 pm from the Ti centre and span an angle of 133.0° at the Ti atom, the two cyclopentadienyl planes intersecting at an angle of 47.2° . This $(C_5H_5)_2Ti$ geometry is almost indistinguishable from that of normal tetracoordinate derivatives, such as $(C_5H_5)_2TiCl_2$ [20].

* Detailed structural data are available on request from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldszentrum 2, by citing of deposit. No. CSD 52002, the authors and the journal reference for this article.

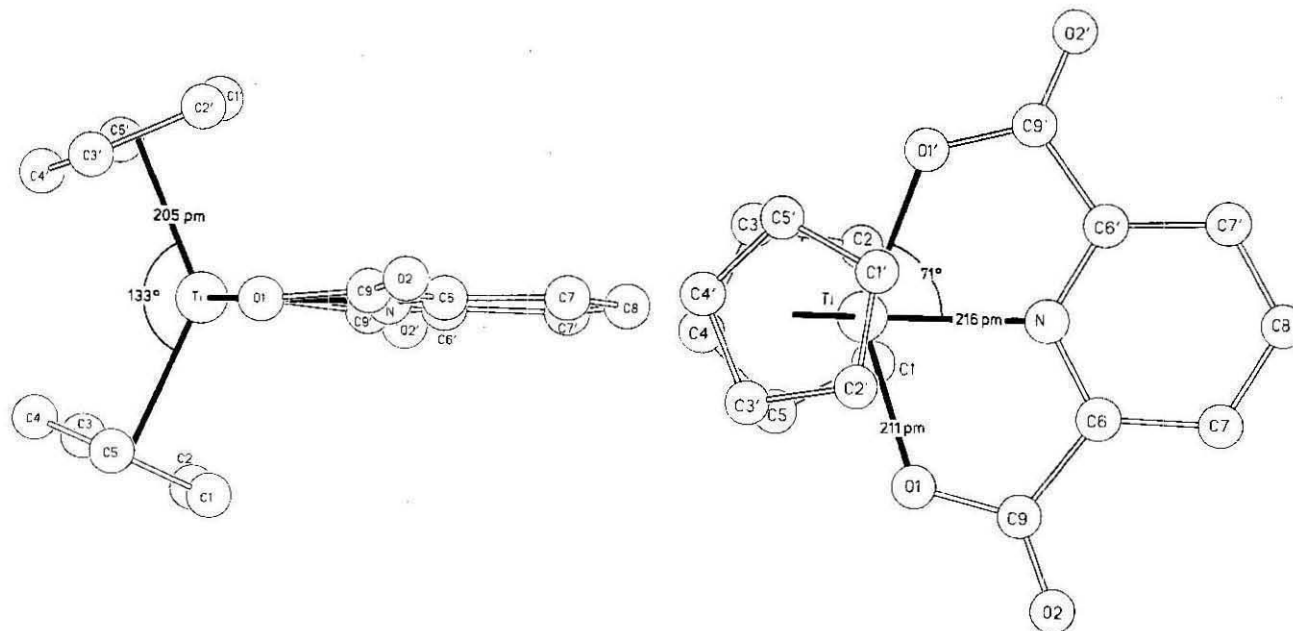


Fig. 1. Molecular structure of $(C_5H_5)_2Ti$ dipicolinate. Projection on to the plane containing the C_5H_5 -ring centroids, the N atom and the Ti centre (left) and onto the $TiO(1)NO(1')$ ligand plane perpendicular to it (right).

As expected from structural studies on other transition metal dipicolinate complexes [21–25], the dipicolinate ligand is bound to the Ti centre by its pyridine N atom and two of the carboxylate O atoms, which occupy the central and the two lateral coordination sites of the titanocene fragment. The Ti–N and Ti–O distances of 216 and 211 pm are significantly longer than Ti–N≡ bonds (196–202 pm) [2,26,27] and Ti–O bonds (186–190 pm) [28–30] in comparable, tetracoordinate titanocene complexes. The O–Ti–N angle of 71.1° is within the range of 65–73° found for other pentacoordinate, non-hydridic metallocene derivatives [10,11].

The Ti centre and its N and O ligand atoms are coplanar by crystal symmetry; the TiO(1)NO(1') plane is perpendicular to the ring centroid–Ti–centroid plane: the two planes intersect at an angle of 89.9°. Interestingly, the plane of the pyridine ring is not quite coplanar with the TiO(1)NO(1') plane: A slight rotational deviation of these two planes by 3.6° is connected with a rotation of both CO₂ groups by 4.8° out of plane of the pyridine ring, and by 7.4° out of the TiO(1)NO(1') plane. A similar deviation from coplanarity, which will lead to a slight shortening of the Ti–N relative to the two Ti–O distances, with respect to a fully coplanar geometry, has been reported for the Ti^{IV} complex (H₂O)₂(O₂)Ti(dipic) [21].

From Fig. 1 it is apparent that the dipicolinate ligand, with its rather small chelate bite angle of about 70°, is almost ideally suited to induce a pentacoordinate geometry even at a (C₅H₅)₂Ti centre, which otherwise appears to avoid this increase in coordination number, probably for steric reasons.

In line with this view, we find that (C₅H₅)₂Ti(dipic) and (CH₃)₄C₂(C₅H₄)₂Ti(dipic) are quite inert to ligand exchange reactions. While tetracoordinate titanocene bis-carboxylates (C₅H₅)₂Ti(OOCR)₂, are rapidly hydrolysed upon contact with water [31], hydrolysis of (C₅H₅)₂Ti(dipic) in mixed aqueous solvents, such as H₂O/THF or H₂O-saturated CHCl₃ proceeds at a remarkably low rate, with half-lives of about 4–5 days at 20°C.

Even conversion into (C₅H₅)₂TiCl₂ by treatment with gaseous HCl in CHCl₃, which is practically instantaneous for other titanocene bis-carboxylate derivatives, requires about 30 min to go to completion with (C₅H₅)₂Ti(dipic). This would indicate that neither associative nor dissociative ligand exchange reaction modes are easily accessible for a rather rigidly connected pentacoordinate species such as (C₅H₅)₂Ti(dipic).

Experimental

All operations were conducted under N₂ in Schlenk-type equipment.

1. (C₅H₅)₂Ti(dipic). A solution of dimethyltitanocene [32], (C₅H₅)₂Ti(CH₃)₂ (416 mg, 2.0 mmol) in 5 ml of dry toluene is slowly added, at room temperature, to a suspension of 334 mg (2.0 mmol) of dipicolinic acid in 50 ml of dry tetrahydrofuran. The mixture is stirred for about 1 h, during which the dipicolinic acid dissolves with evolution of CH₄, to form a clear orange solution. The solution is evaporated to dryness and the residue taken up in ca. 15 ml of toluene. After addition of hexane to the point of precipitation, and cooling to –80°C, 423 mg (62% theoretical yield) of (C₅H₅)₂Ti(dipic) are obtained as a yellow powder, which is quite soluble in CHCl₃, toluene or THF. The material is identified from its ¹H NMR spectrum (Table 1), its mass spectrum (with molecular ion at *m/e* 343 and appropriate isotope distribution), and by its crystal and molecular structure.

2. $C_2(CH_3)_4(C_5H_4)_2Ti(dipic)$. An analogous reaction starting from 290 mg (1 mmol) $C_2(CH_3)_4(C_5H_4)_2Ti(CH_3)_2$ [33] and 167 mg (1 mmol) dipicolinic acid yields 493 mg (58% theoretical yield) of $C_2(CH_3)_4(C_5H_4)_2Ti(dipic)$. Identification is from its 1H NMR (Table 1), and mass spectra (molecular ion at m/e 425).

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