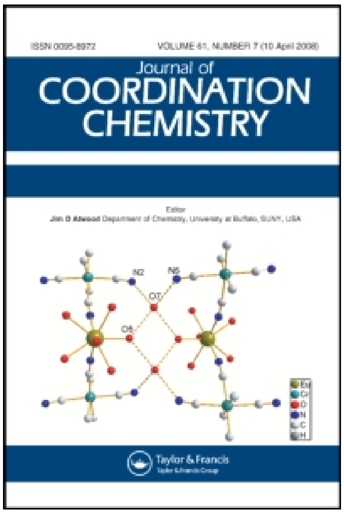

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Synthesis and characterization of two <i>bis</i>(η^5-methylcyclopentadienyl)hydroxynaphthoatotitanium complexes

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Synthesis and characterization of two *bis*(η^5-methylcyclopentadienyl)hydroxynaphthoatotitanium complexes

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Based on the reaction of *bis*(η^5-methylcyclopentadienyl) dichlorotitanium (Cp'_2TiCl_2, $Cp' = \eta^5$-C_5H_4Me) with 3-hydroxy-2-naphthoic acid (HNA-1) and 1-hydroxy-2-naphthoic acid (HNA-2), in the presence of β-cyclodextrin polymer (β-CDP) as a catalyst, two titanocene complexes: *bis*(η^5-methylcyclopentadienyl) 3-hydroxy-2-naphthoatotitanium (**1**) and *bis*(η^5-methylcyclopentadienyl)1-hydroxy-2-naphthoatotitanium (**2**), were synthesized and characterized by elemental analysis, IR and ^1H NMR spectra. X-ray diffraction analysis of **1** and **2** show mononuclear Ti^{IV} and indicate that the geometries at titanium are distorted tetrahedra with coordination number four. Both complexes exhibit 3-D frameworks constructed through H-bonding and $C–H \cdots \pi$ interactions. There are no π–π stacking interactions between the naphthyl rings and cyclopentadienyl rings of **1**, while there are three types of π–π interactions in the structure of **2**, owing to their different hydroxyl position in naphthalene rings.

Keywords: Titanocene complex; Crystal structure; 3-Hydroxy-2-naphthoic acid; 1-Hydroxy-2-naphthoic acid

1. Introduction

Since Köpf and Köpf-Maier showed that Cp_2TiCl_2 is highly active against a variety of tumor cells, titanocene derivatives have received considerable attention, and a large family of derivatives has been synthesized [1–5]. Substituted salicylic acids possess anti-inflammatory activity and are also of interest from a structural point of view, so synthesis of substituted salicylate methylcyclopentadienyl titanocene derivatives may develop new anticancer medicines with a synergistic effect or novel molecular structures of titanium aryloxides. There are very few structural characterizations of substituted salicylate titanocene complexes [6, 7], and even few of aromatic acid methylcyclopentadienyl titanocene derivatives [8].

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In the previous work, we have synthesized and characterized some substituted salicylate titanocene derivatives in aqueous media; the reaction is strongly affected by temperature, pH of the aqueous solution, concentration of substituted salicylic acid, and the ratio of reacting species [9]. A new approach was reported recently for synthesizing titanocene derivatives catalyzed by β-CDP based on the concept of enhancing the ability to form complex ligands (figure 1) [10]. As a result, β-CDP not only enhanced the stability of titanocene (Cp_2Ti) derivatives and accelerated the reaction speed, but also improved the yield. In this article, two new titanocene derivatives **1** and **2** have been prepared in the presence of β-CDP in $CHCl_3$, further proving the feasibility of supramolecular catalytic reactions in synthesizing titanocene derivatives.

Molecular structures of substituted salicylate titanocene complexes exhibit interesting structural variations [11]. Herein, we are interested in titanocene complex structures when using similar ligands such as HNA-1 and HNA-2. The experimental results show that both **1** and **2** consist of 3-D networks formed by weak interactions. However, the different position of hydroxyl of their ligands leads to different structures.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were analytical reagent grade; acetyl acetone, β-cyclodextrin (β-CD), HNA-1 and HNA-2, were used directly without purification. Dichloromethane and hexane were dried before use. Cp'_2TiCl_2 and β-CDP were prepared by methods reported in the literature [12, 13]. IR spectra were recorded as KBr pellets on an EQUINX55 spectrometer. The ^{1}H NMR spectra were recorded on an AVANCE 300 MHZ with TMS as internal standard and $CDCl_3$ as solvent. Elemental analyses were determined using a Vario EL III elemental analyzer. All measurements were performed at room temperature.

2.2. *Synthises of 1 and 2*

β-cyclodextrin polymer (2.2 g) was ground into fine powder, immersed in water for 1–2 h and then filtered. The solid was added into a solution of Cp'_2TiCl_2 (2.0 mmol) and

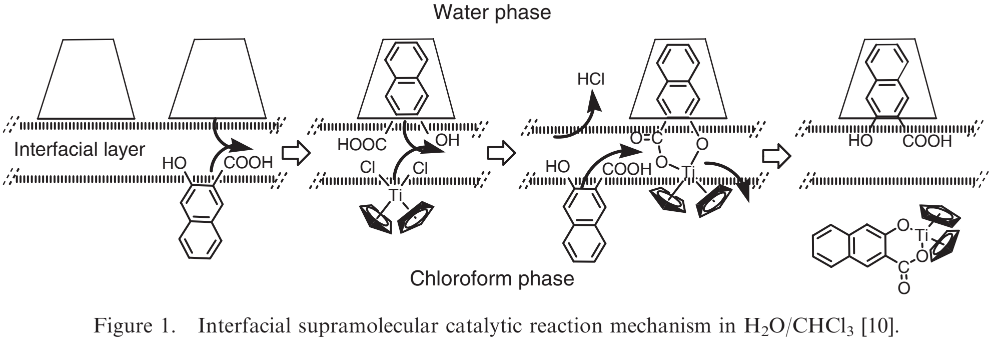


Figure 1. Interfacial supramolecular catalytic reaction mechanism in $H_2O/CHCl_3$ [10].

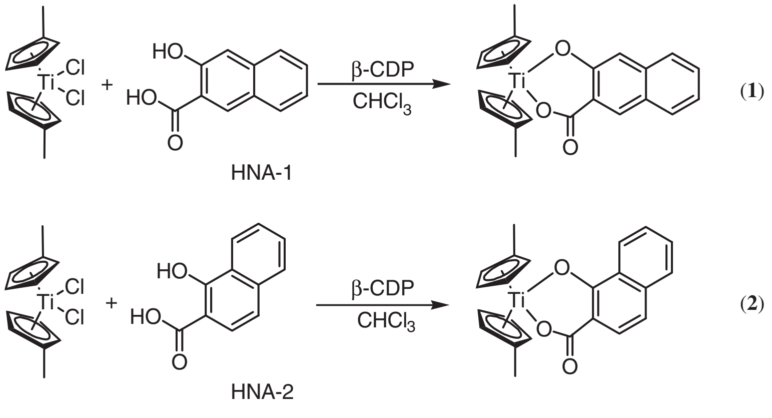
HNA-1 or HNA-2 (2.2 mmol) in 30 mL chloroform. The reaction mixture was stirred for 0.5 h at room temperature to give a deep red solution (brown solution for **2**). The resulting solution was separated and washed with an aqueous solution of saturated sodium carbonate and then water, dried over anhydrous magnesium sulfate and then filtered. The filtrate was evaporated to dryness under vacuum [9]. The solid products were recrystallized with dichloromethane–hexane at low temperature to give titanocene complexes **1** and **2**. The preparation of the complexes was expressed as scheme 1.

Complex 1: Deep red, sheet-like crystalline solid (0.64 g, 81.8%). m.p.: 149–151°C; Anal. Calcd for $C_{23}H_{20}O_3Ti$ (%): C, 70.42; H, 5.14. Found: C, 70.88; H, 4.81. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.04 (6H, s, $2 \times CH_3$), 6.04–6.08 (4H, q, C_5H_4), 6.40–6.52 (4H, q, C_5H_4), 7.00 (1H, s, ArH), 7.27–7.33 (1H, q, ArH), 7.45 (1H, t, ArH), 7.65–7.68 (1H, d, ArH), 7.86–7.90 (1H, d, ArH), 8.82 (1H, s, ArH). IR (KBr) ν: 3085, 2915, 1617, 1583, 1442, 1340, 1278, 1249, 1212, 1164, 1067, 1033, 916, and 824 cm^{-1}.

Complex 2: Brown, sheet-like crystalline solid (0.63 g, 79.9%). m.p.: 196–198°C; Anal. Calcd for $C_{23}H_{20}O_3Ti$ (%): C, 70.42; H, 5.14. Found: C, 70.18; H, 4.94. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.01 (6H, s, $2 \times CH_3$), 6.08–6.16 (4H, d, C_5H_4), 6.43–6.53 (4H, q, C_5H_4), 7.30–7.34 (1H, d, ArH), 7.40–7.45 (1H, t, ArH), 7.52–7.57 (1H, t, ArH), 7.78–7.82 (1H, d, ArH), 8.11–8.14 (1H, d, ArH), 8.21–8.24 (1H, d, ArH). IR (KBr) ν: 3086, 2909, 1604, 1500, 1396, 1341, 1236, 1136, 1079, and 803 cm^{-1}.

2.3. *X-ray crystallography*

Crystals of **1** and **2** suitable for X-ray diffraction were obtained from dichloromethane–hexane solution at low temperature for 2 weeks. The complexes were sheet-like crystals, remarkably stable in air. Data collection was performed on a Bruker Smart-1000 CCD detector using graphite-monochromated Mo-Kα radiation (ω-2θ scans, $\lambda = 0.71073$ Å) at room temperature. The structures were solved by direct methods and refined on F^2 by full matrix least-squares with Bruker's SHEXTL-97 program [14]. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding mode. The crystals used for diffraction showed no decomposition during data collection. The crystal data, experimental details, and



Scheme 1. The preparation process of **1** and **2**.

refinement results are presented in table 1. The selected bond lengths and angles of **1** and **2** are listed in table 2.

3. Results and discussion

3.1. *Synthesis and characterization*

The methylcyclopentadienyl titanocene complexes **1** and **2** were synthesized at room temperature in good yields in the presence of β-CDP. Based on our previous work [10], the reaction mechanism was proposed in figure 1. β-CDP is the supramolecular receptor and a reversible reaction occurs first between the β-CDP and the ligand to give a supramolecular complex. Then, the activated ligand of the supramolecular complex reacts interfacially with Cp'_2TiCl_2 to form an intermediate supramolecular titanocene complex. Finally, the next ligand substitutes for the titanocene complex and enters the supramolecular receptor, allowing the reaction to continue.

Complexes **1** and **2** were characterized by IR and ^{1}H NMR, respectively. IR spectra show bands at 2915 cm^{-1}, **1**, and 2909 cm^{-1}, **2**, assigned to $\nu(CH_3)$ of Cp′, and Cp′ rings at 3085, 1442, 1033, 824 cm^{-1} and 3086, 1396, 1079, 803 cm^{-1} for **1** and **2**, respectively. In addition, strong bands at 1617 and 1340 cm^{-1} for **1**, and 1604 and 1341 cm^{-1} for **2**, are assigned to $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$ bands of a carboxylate. The $\Delta\nu(\nu_{asym-}\nu_{sym})$ is used to determine the coordination mode of the carboxylate and the metal with $\Delta\nu$

Table 1. Crystallographic data for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{23}H_{20}O_3Ti$	$C_{23}H_{20}O_3Ti$
Formula weight	392.29	392.29
Temperature (K)	273(2)	296(2)
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
Units of dimension (Å, °)		
a	22.8047(12)	7.7890(6)
b	12.9051(7)	8.2590(7)
c	12.5893(7)	15.6185(13)
α	90	85.973(2)
β	97.4100(10)	83.653(2)
γ	90	65.6480(10)
V (Å^3)	3674.1 (3)	909.39(13)
Z	6	2
D_{Calcd} ($g\,cm^{-3}$)	1.319	1.433
μ (mm^{-1})	0.394	0.491
$F(000)$	1512	408
Crystal dimensions (mm^3)	$0.36 \times 0.24 \times 0.11$	$0.40 \times 0.21 \times 0.08$
λ(Mo-Kα) (Å)	0.71073	0.71073
2θ range (°)	1.82–25.10	2.63–25.10
S on F^2	1.064	1.025
Total/unique/R_{int}	9176/3276/0.0282	4710/3195/0.0264
R_1, wR_2 [$I > 2\sigma(I)$]	0.0454, 0.1142	0.0488, 0.1143
R_1, wR_2 (all data)	0.0716, 0.1234	0.0860, 0.1264
$\Delta\rho_{min\ and\ max}$ (e Å^{-3})	0.421 and −0.297	0.250 and −0.289

below 200 cm^{-1} for bidentate carboxylate and above 200 cm^{-1} for monodentate carboxylate [9]. The $\Delta\nu$ in the complexes are 277 cm^{-1} for **1** and 263 cm^{-1} for **2**, pointing to monodentate carboxylate, consistent with their crystal structures as described below.

The ^{1}H NMR spectra of **1** and **2** show two sets of signals for the Cp′ ring and the naphthalene ring protons, as well as the CH_3. Hydroxyl signals were not observed, indicating that both the hydroxyl and carboxyl are coordinated with Ti, consistent with IR analysis and their solid-state structures.

3.2. *Molecular and crystal structures of 1 and 2*

Complex **1** crystallizes in the monoclinic space group $C2/c$ with $Z = 6$ formula units in the unit cell. As shown in figure 2, the Ti^{IV} is mononuclear, surrounded by two methylcyclopentadienyl moieties and one oxygen of hydroxyl and one carboxyl oxygen of HNA-1. HNA-1 is a bidentate ligand coordinating with Ti^{IV} to form a hexacyclic complex. The geometry of the titanocene skeleton of **1** is similar to other titanocene complexes with respect to bond distances and angles [11]. The pseudotetrahedral arrangement about titanium has a large Cp′1–Ti–Cp′2 angle [132.11(10)°] and small O1–Ti–O2 angle [87.53(8)°]. The O–Ti–O angle is somewhat smaller than that of $Cp_2Ti(O,O')(OCC_6H_4)$[O–Ti–O = 88.3(2)°] [7], $[Cp_2Ti(OOCCF_3)]_2(\mu\text{-}O)$ [O–Ti–O = 89.7(2)°] [15] and $Cp_2Ti(O_2CCH_2CN)_2$ [O–Ti–O = 89.3(2)°] [16], but larger than that of $Cp_2Ti(C_2O_4)$ [O–Ti–O = 79.4°] [17], indicating the naphthalene effects the molecular structure of **1**.

Analysis of the crystal packing of **1** shows complicated intermolecular hydrogen bonds and C–H $\cdots$ π interactions. Figure 3 shows the three C–H $\cdots$ O hydrogen bonds via [C19–H19 $\cdots$ O1, C16–H16 $\cdots$ O2, and C13–H13 $\cdots$ O3], linking the adjacent molecules to form a 1-D zigzag chain. A stepwise layer is further directed along the bc-direction by hydrogen bonds C12–H12 $\cdots$ O3 and C17–H17 $\cdots$ O3

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Ti1–O1	1.957(19)	Ti1–O1	1.937(2)
Ti1–O2	1.909(19)	Ti1–O2	1.915(2)
Ti1–Cp′1	2.076(16)	Ti1–Cp′1	2.057(2)
Ti1–Cp′2	2.072(2)	Ti1–Cp′2	2.070(19)
O1–C11	1.293(3)	O1–C11	1.308(4)
O3–C11	1.222(3)	O3–C11	1.221(4)
Cp′1–Ti1–Cp′2	132.11(10)	Cp′1–Ti1–Cp′2	133.23(9)
Cp′1–Ti1–O1	107.38(7)	Cp′1–Ti1–O1	108.07(10)
Cp′1–Ti1–O2	108.78(7)	Cp′1–Ti1–O2	107.89(10)
Cp′2–Ti1–O1	105.79(10)	Cp′2–Ti1–O1	105.39(9)
Cp′2–Ti1–O2	106.19(11)	Cp′2–Ti1–O2	105.31(10)
O2–Ti1–O1	87.54(8)	O1–Ti1–O2	87.45(10)
C11–O1–Ti1	132.86(17)	C11–O1–Ti1	128.3(2)
C8–O2–Ti1	125.38(16)	C10–O2–Ti1	128.3(2)
O2–C8–C9	120.70(2)	O1–C11–C9	117.3(3)
O1–C11–C9	117.60(2)	O2–C10–C9	123.1(3)

Notes: Cp′, the centroid of the MeC_5 ring: Cp′1 (C12–C16) and Cp′2 (C17–C21, **1**), (C18–C22, **2**), respectively.

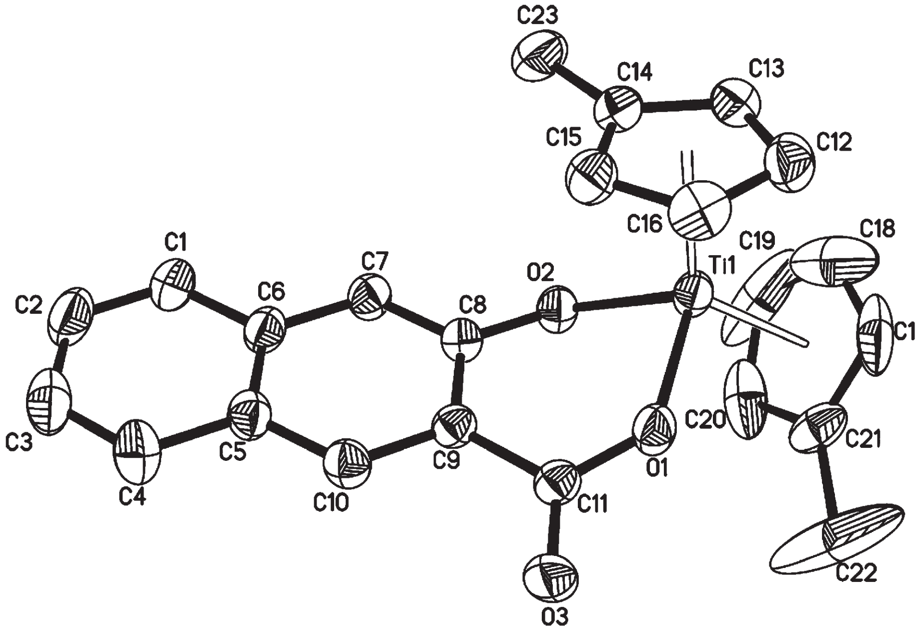


Figure 2. Molecular structure of **1**. Thermal ellipsoids are shown at the 30% level, hydrogen atoms are omitted for clarity.

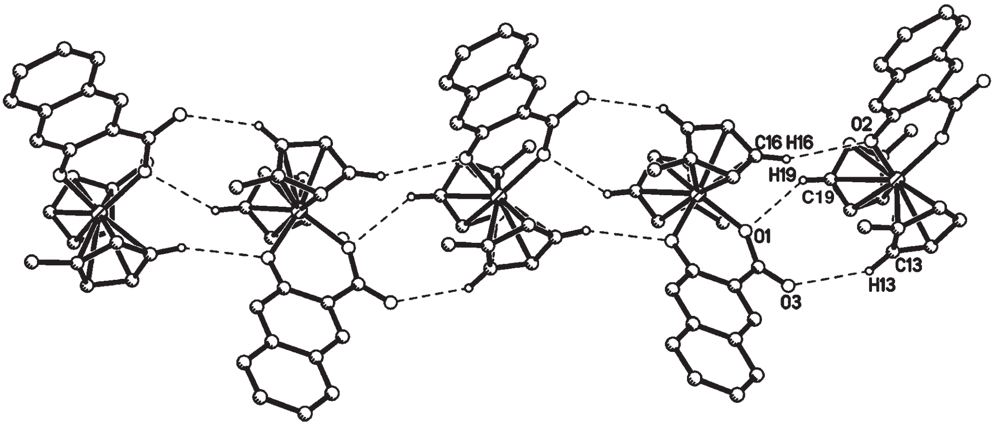


Figure 3. Intermolecular hydrogen bonding of **1**. The zigzag chains are assembled by hydrogen bonds C19–H19···O1, C16–H16···O2, and C13–H13···O3.

(supplementary material). The most interesting feature of **1** is its 3-D butterfly network formed by intermolecular C–H···π interactions [18] C3–H3···Cp′2, C22–H22A···Ph2, C23–H23A···Ph1 and C23–H23A···Ph2 together with C3···C4 interaction (supplementary material), where Ph1 represents the centroids of the C1–C6 rings and Ph2 is that of the C5–C10 rings in the same naphthalene rings. The 3-D supramolecular framework consists of 1-D roughly square channels, and the corresponding distance between C3 and C4 is 3.389 Å, within the normal range compared with the reported criteria 3.40 Å of C···C interaction. There are no π–π stacking interactions between naphthalene rings and Cp′ rings in the packing diagram (supplementary material). The Ph1 ring of one molecule and Ph1* of a neighboring molecule are almost parallel, with a dihedral angle between them of 0.02° and a distance between their centroids of 4.002 Å, which is too long [19]. Hydrogen bonding and C–H···π interactions contribute to forming the 3-D supramolecular framework.

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ with $Z=2$. The asymmetric unit contains one titanium, two methylcyclopentadienyl rings and one HNA-2 ligand forming a distorted tetrahedral structure (figure 4), similar to that of **1**. The Ti–C distances are in the range from 2.329 to 2.442 Å; selected bond lengths and angles are listed in table 2. The Ti–Cp′2 distance [2.070(19) Å] is somewhat longer than that of Ti–Cp′1 [2.057(2) Å], and the Ti–O2 [1.915(2) Å] distance is shorter than that of Ti–O1 [1.937(2) Å]. The Cp′1–Ti1–Cp′2 angle is 133.23(9)° and O1–Ti1–O2 = 87.45(10)°.

The vicinal molecules are connected into a 1-D band chain by hydrogen bonds C13–H13···O1, C14–H14···O3, C15–H15···O3, C18–H18···O3, and C19–H19···O3, while π–π stacking interactions expand the 1-D chain to a 2-D infinite stepwise structure (supplementary material). The peculiarity of **2** is its 3-D supramolecular network, which is linked by C–H···π interactions C12–H12···Cp2, C23–H23C···Ph1, and C23–H23C···Ph2 [19] together with π–π stacking. The dihedral angle between Ph1 of one molecule and Ph1* of a neighboring molecule is 0.02°, and the dihedral angle between Ph1 and Ph2* of a neighboring one is 1.10°, both almost parallel (supplementary material). The corresponding Ph1···Ph1* distance is 3.618(3) Å and Ph1···Ph2* is 3.787(3) Å, indicating that π–π stacking exists in **2** [19, 20]. In addition, the Cp1 of one molecule and Cp1* of a neighboring molecule are absolutely parallel (supplementary material), and the corresponding Cp1···Cp1* distance is 3.789(3) Å, denoting there is another π–π stacking in **2**. Obviously, strong hydrogen bonding interactions play an important role in the formation of the 3-D supramolecular framework (figure 5, and supplementary material) while π–π stacking interactions between the naphthalene rings of the ligand and methylcyclopentadienyl rings also play a definite role in stabilizing the whole crystal structure.

3.3. *Structure comparison*

As shown in table 1, **1** crystallized in the monoclinic system with space group $C2/c$ while **2** crystallized in the triclinic system with space group $P\bar{1}$. Both of the *bis*(η5-methylcyclopentadienyl) titanium fragments have typically bent sandwich geometries and titanium atoms are in pseudotetrahedral environments. The distances of Ti1–Cp′1 [2.076(16) Å] and Ti1–Cp′2 [2.072(2) Å] in **1** are different from that of [2.057(2) Å] and [2.070(19) Å] in **2**. The difference of O–C bond lengths of carboxyl between O1–C11 [1.293(3) Å] and O3–C11 [1.222(3) Å] is 0.071 Å for **1** and 0.087 Å for **2**, in agreement with literature: $Cp_2Ti(C_2O_4)$ (0.082 Å) [17] and $Cp_2Ti(O,O')(OCC_6H_4)$ (0.083 Å), demonstrating monodentate HNA-1 and HNA-2 [7]. The crystal structure parameters of **1** and **2**, and reported substituted salicylic titanocene complexes are shown in table 3. All the titanocene complexes belong to a monoclinic crystal system except for **2**. The observed Ti–O bond lengths in these complexes are substantially shorter than a typical single Ti–O bond of ca 2.0 Å, and Cp′–Ti–Cp′ angles are smaller than typical Cp–Ti–Cp angles (136°) [2]. The O–Ti–O and Cp′–Ti–Cp′ angles of these

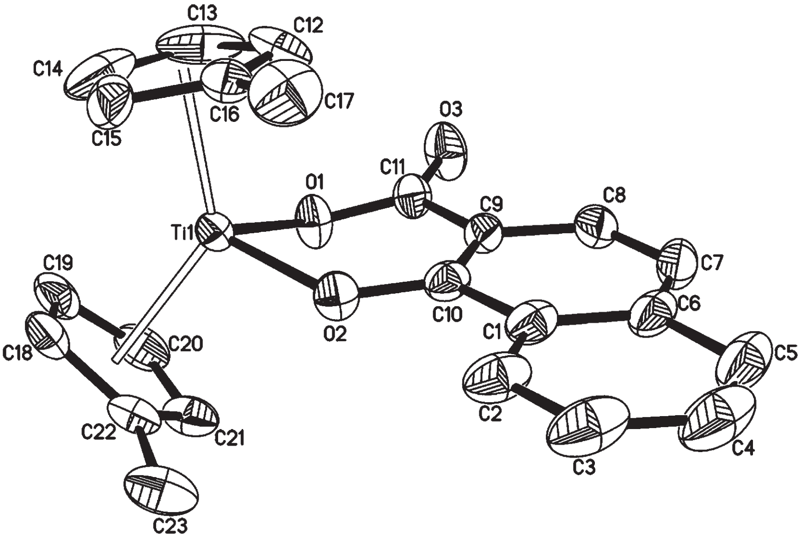


Figure 4. Molecular structure of **2**. Thermal ellipsoids are shown at the 30% level, hydrogen atoms are omitted for clarity.

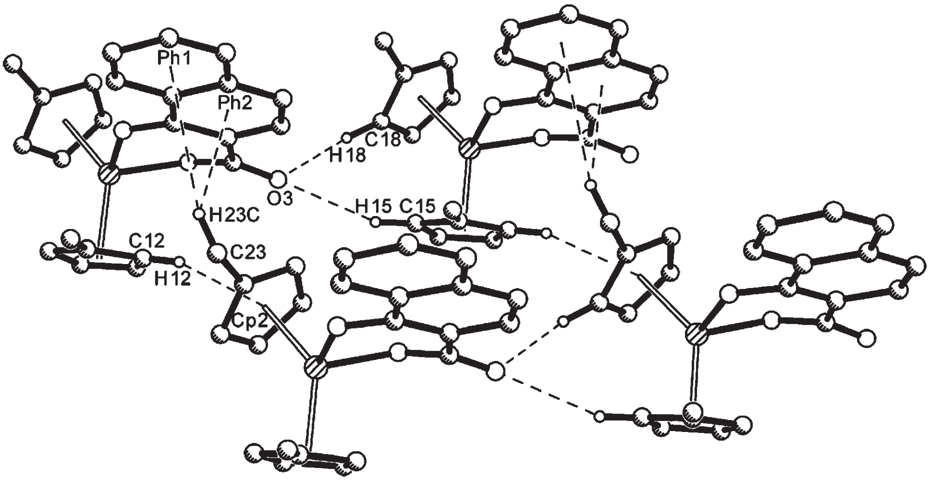


Figure 5. Part of the crystal structure of **2**. A 3-D network structure strongly stabilized by complicated intermolecular hydrogen bonds and π–π stacking interactions.

complexes are close, the coordinate number of each titanium is the same, and each complex exhibits a distorted tetrahedral structure. Each substituted salicylic acid is bidentate forming a cyclic complex.

The different position of hydroxyl in the naphthalene ring significantly influences the weak interactions as well as the specific framework structures, although HNA-1 and HNA-2 are salicylic-like chelating reagents.

Table 3. Structural comparisons of **1** and **2** and salicylato titanocene derivatives.

Name	**1**	**2**	$Cp_2Ti(O,O')$ $(5\text{-}NO_2\text{–}OCC_6H_3)$ [11]	$Cp_2Ti(O,O')$– (OCC_6H_4) [7]
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	6	2	4	4
Ti–O (Å)	1.9570(19) 1.9090(18)	1.937(2) 1.915(2)	1.954(4) 1.936(3)	1.915(4) 1.949(4)
O–Ti–O (°)	87.53(8)	87.46(9)	87.34	88.3(2)
Cp′–Ti–Cp′/Cp–Ti–Cp (°)	132.11(10)	133.23(9)	132.05	133.6

4. Conclusion

In the study two titanocene complexes, 3-hydroxy-2-naphthoic dimethyltitanocene and 1-hydroxy-2-naphthoic dimethyltitanocene, have been synthesized in $CHCl_3$ system catalyzed by β-CDP; both contain naphthalene backbones and exhibit 3-D frameworks constructed through weak interactions. They differed when forming the 3-D network structures because of their different hydroxyl position at naphthalene rings.

Supplementary data

Crystallographic data (excluding structure factors) reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication. CCDC numbers are 614688 and 689214 for **1** and **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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