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Syntheses and supramolecular structures of two 5-nitrosalicylate titanocene complexes

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Two 4-coordinated titanocene complexes, $[(\eta^5\text{-}C_5H_5)_2Ti(O,O')(5\text{-}NO_2\text{-}OCC_6H_3)]$ (I) and $[(\eta^5\text{-}C_5H_5)_2Ti(2\text{-}OH\text{-}5\text{-}NO_2\text{-}O_2CC_6H_3)_2]$ (II), have been synthesized by reaction of Cp_2TiCl_2 and 5-nitrosalicylic acid in aqueous media. Single-crystal X-ray analyses of I and II display the mononuclear forms of Ti^{IV}, and geometries at titanium atoms are distorted tetrahedrons, while the coordination environment at Ti^{IV} in complex I is different from that in complex II. Crystallographic characterization revealed that each of the complexes exhibits a three-dimensional framework constructed through weak interactions, which are H-bonding, π–π stacking and C–H$\cdots\pi$ interactions, but they differ greatly when forming the three-dimensional network structure in both complexes. The results show that the dramatic change of conditions has great effect on the molecular structure of 5-nitrosalicylate titanocene, thereby significantly influencing the weak interactions and the specific framework structure.

KEYWORDS: titanocene complexes; cyclopentadienyl; 5-nitrosalicylic acid; crystal structure

INTRODUCTION

The past two decades have witnessed the development of a large number of titanocene derivatives owing to their ability to catalyse the polymerization of olefinic monomers,[1–4] and hydrogenation and isomerization,[5–8] as well as their antitumor activity[9]. Thus, a variety of titanocene derivatives have been prepared, in which Ti^{IV} is known to exist as mononuclear,[10–16] binuclear,[17–19] trinuclear[20,21] and tetranuclear[22,23] forms. Salicylic acid derivatives occupy an important position in plant disease resistance owing to their antibiotic function of diminishing inflammation,[24–26] so the synthesis of substituted salicylate titanocene derivatives might develop new anticancer medicines with a synergistic effect. In addition, the rational design of supramolecular polymeric architectures has attracted considerable interest from chemists, not only because of their intrinsic esthetic appeal, but also because of their potentially exploitable properties.[27,28] Supramolecular assemblies have received considerable attention in recent years, including one-dimensional,[29,30] two-dimensional[31,32] and three-dimensional networks,[33,34] which have been synthesized by a combination of covalent bond formation and supramolecular interactions, including hydrogen bonds, π–π stacking and M$\cdots$X (X = S, O, I) contacts. Hydrogen bonds and π–π stacking interactions are an important research content in the supramolecular chemistry and crystal engineering.[35,36] Meanwhile, a still weaker molecular force, the C–H$\cdots\pi$ interaction, has been recognized to play a substantial role in a variety of chemical and biological phenomena.[37] They have contributed significantly to self-assembly and molecular recognition processes.[38] However, the structural characterizations of substituted salicylate titanocene are still comparatively scarce.[39]

Here, we report the synthesis and structure of complexes, $[(\eta^5\text{-}C_5H_5)_2Ti(O,O')(5\text{-}NO_2\text{-}OCC_6H_3)]$ (**I**) and $[(\eta^5\text{-}C_5H_5)_2Ti(2\text{-}OH\text{-}5\text{-}NO_2\text{-}O_2CC_6H_3)]_2$ (**II**). These complexes were characterized by elemental analysis, IR, ^1H NMR spectroscopy and X-ray diffraction analyses. There are significant differences between the two complexes. In complex **I**

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the Ti^{IV} is mononuclear and is surrounded by two cyclopentadienyls, one oxygen atom of hydroxyl and one carboxy oxygen atom of 5-nitrosalicylate. 5-Nitrosalicylate acts as bidentate ligand and coordinates with Ti^{IV}. In complex **II** the Ti^{IV} is mononuclear and is surrounded by two cyclopentadienyl moieties and two carboxy oxygen atoms of two 5-nitrosalicylates. Each 5-nitrosalicylate acts as a unidentate ligand and coordinates with Ti^{IV}. The determination results show that there is a variety of weak intermolecular forces, such as hydrogen bonds, π–π stacking and C–H$\cdots\pi$ interactions in complexes **I** and **II**. Hydrogen bonds in complex **I** link the adjacent molecules to form a one-dimensional linear chain, while π–π stacking and C–H$\cdots\pi$ interactions link the adjacent linear chains to form a three-dimensional network structure. The complicated intermolecular hydrogen bonds in complex **II** contribute to the construction of its three-dimensional network structure and π–π stacking together with C–H$\cdots\pi$ interactions consolidate the supramolecular structure.

RESULTS AND DISCUSSION

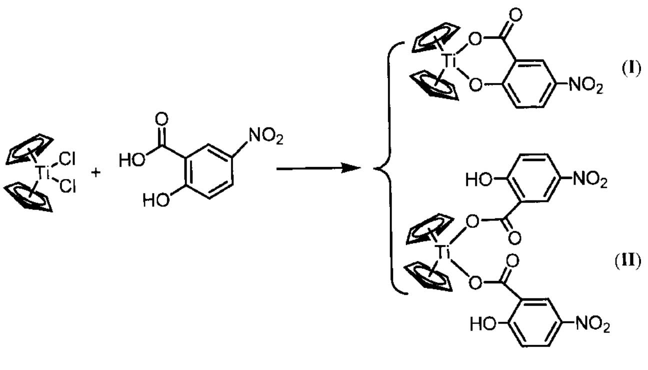
When the reaction mixture was carried out in varying conditions, such as time, pH values and proportion of titanocene dichloride and 5-nitrosalicylic acid, two different titanocene derivatives were obtained. In complex **I**, 5-nitrosalicylate acted as a bidentate ligand and coordinated with Ti^{IV} to form a cyclic compound. In complex **II**, two 5-nitrosalicylates acted as unidentate ligands and coordinated with Ti^{IV}, similar to $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5\text{-}2\text{-}OH)_2$.[39] Two hydroxy oxygen atoms did not coordinate with Ti^{IV} but formed two stable hexagons by O–H$\cdots$O intramolecular hydrogen bonds with adjacent oxygen atoms, in which atoms O2 and O7 act as acceptors, and the two donors are O3, via atoms H3 and O8, via atom H8.[40] Details of the hydrogen bonding are given in Table 1. The preparation process of complexes **I** and **II** are shown in Scheme 1.

Molecular and crystal structure of I

A perspective view of the structure of **I** with the atom numbering scheme is given in Fig. 1. In complex **I**, the Ti^{IV} is mononuclear and is surrounded by two cyclopentadienyl moieties and one oxygen atom of hydroxyl and one carboxy oxygen atom of 5-nitrosalicylate. 5-Nitrosalicylate acts as a bidentate ligand and coordinates with Ti^{IV} to form a hexacyclic compound. The coordination environment at titanium can be described as pseudotetrahedral with the large Cp1–Ti–Cp2 angle (132.05°) and small O3–Ti–O1 angle [87.34(12)°] owing to the size difference between Cp ligands and O atoms. The Ti–Cp1 distance (2.0509 Å) is somewhat longer than that of Ti–Cp2 (2.0335 Å), and the Ti–O1 [1.954(4) Å] distance is longer than that of Ti–O3 [1.936(3) Å]. Selected bond lengths and angles are listed in Table 2. Furthermore, two C–H$\cdots$O hydrogen bonds via [C11–H11$\cdots$O2 and C12–H12$\cdots$O5] (Table 1), link the adjacent molecules to form a one-dimensional linear chain (Fig. 2). The phenyl ring of one molecule and a neighbouring molecule are almost parallel, with a dihedral angle between them of 0.02°, and the corresponding Ph$\cdots$Ph# distance is 3.718 Å[41,42] (where Ph and Ph# represent the centroids of the phenyl ring C12–C17), indicating that weak π–π stacking interactions exist in complex **I**. The double chains are connected through extensive π–π stacking interactions, hence generating a two-dimensional network. Moreover, the adjacent pairs of 5-nitrosalicylate titanocene are tied by another intermolecular C–H$\cdots\pi$ interaction (Fig. 3) with C13–H13$\cdots$Ph (3.270 Å),[37,43] where Ph is the center of gravity of the phenyl ring. The C–H$\cdots\pi$ interactions make the 5-nitrosalicylate titanocene to form a three-dimensional network structure (Fig. 4).

Table 1. Hydrogen bond lengths (Å) and angles (deg) for complexes **I** and **II**

	D–H$\cdots$A	d (D–H)	d (H$\cdots$A)	d (D$\cdots$A)	(DHA)
I	C11–H11$\cdots$O2	0.980	2.367	3.308	160
	C12–H12$\cdots$O5	0.980	2.55	3.502	163
II	O3–H3$\cdots$O2	0.820	1.818	2.546	147
	O8–H8$\cdots$O7	0.820	1.798	2.532	148
	C4–H4$\cdots$O7	0.930	2.54	3.455	167
	C14–H14$\cdots$O2	0.930	2.47	3.397	174
	C15–H15$\cdots$O4	0.930	2.51	3.406	161
	C16–H16$\cdots$O7	0.930	2.56	3.172	123
	C16–H16$\cdots$O8	0.930	2.59	3.407	147
	C18–H18$\cdots$O9	0.930	2.60	3.339	137
	C23–H23$\cdots$O3	0.930	2.46	3.370	167
	C24–H24$\cdots$O8	0.930	2.52	3.218	132



Scheme 1. The preparation process of complexes **I** and **II**.

Molecular and crystal structure of II

Figure 5 shows the molecular structure with the atom-labeling scheme and the detailed coordination sphere around the titanium atom. In complex **II**, the Ti^{IV} is mononuclear and

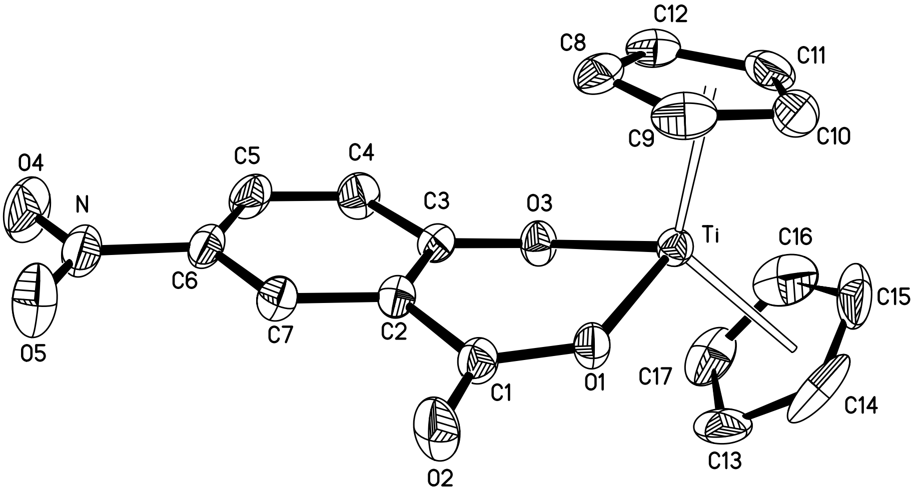


Figure 1. Molecular structure of complex **I** in the crystal with thermal ellipsoids at 30% probability; hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II**

I		II	
Ti–O1	1.954(4)	Ti–O1	1.999(2)
Ti–O3	1.936(3)	Ti–O6	1.951(2)
Ti–Cp1	2.0509	Ti–Cp1	2.0515
Ti–Cp2	2.0335	Ti–Cp2	2.0517
Ti–C8	2.387(5)	Ti–C15	2.372(4)
Ti–C9	2.397(5)	Ti–C16	2.364(4)
Ti–C10	2.352(5)	Ti–C17	2.338(4)
Ti–C11	2.342(5)	Ti–C18	2.322(4)
Ti–C12	2.365(5)	Ti–C19	2.357(4)
Ti–C13	2.355(5)	Ti–C20	2.362(4)
Ti–C14	2.344(6)	Ti–C21	2.371(4)
Ti–C15	2.327(6)	Ti–C22	2.359(4)
Ti–C16	2.323(5)	Ti–C23	2.351(3)
Ti–C17	2.352(5)	Ti–C24	2.359(4)
C1–O1	1.295(5)	C1–O1	1.294(3)
C1–O2	1.209(5)	C1–O2	1.232(3)
O1–Ti–O3	87.34(12)	O6–C8	1.290(4)
Cp1–Ti–Cp2	132.05	O7–C8	1.242(3)
C1–O1–Ti	133.3(3)		
C3–O3–Ti	126.4(2)		
O1–C1–C2	117.0(4)	O1–Ti–O6	95.80
C2–C3–O3	123.4(4)	Cp1–Ti–Cp2	131.93
C1–C2–C3	123.3(4)		

Cp1 are the centroids of the C_5 rings C8–C12 and C15–C19 and Cp2 are the centroids of the C_5 rings C13–C17 and C20–C24, respectively.

is surrounded by two cyclopentadienyls and two carboxy oxygen atoms of two 5-nitrosalicylates. Each 5-nitrosalicylate acts as a unidentate ligand and coordinates with Ti^{IV}. The coordination environment at titanium is similar to that of complex **I**. The Ti–C distances, which vary slightly from 2.322 to 2.372 Å, and the distances from the Ti atom to the Cp1 (2.0517 Å) and Cp2 (2.0515 Å) (Table 2) are in excellent agreement with the corresponding distances in other $(\eta^5\text{-}C_5H_5)_2Ti^{IV}$ structures.[44–48] Furthermore, the presence of two intramolecular hydrogen bonds [C14–H14 $\cdots$ O2 and C16–H16 $\cdots$ O7] contributes to the formation of a 10-membered ring and a six-membered ring in the molecular structure of **II**. The complicated intermolecular hydrogen bonds (Table 1) link two adjacent molecules of 5-nitrosalicylate titanocene to form an infinite two-dimensional network structure (Fig. 6), and further a three-dimensional network structure (Fig. 7). Two phenyl rings of one molecule are almost coplanar. The dihedral angle between them is 4.55°, different from $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5\text{-}2\text{-}OH)_2$ (0°)[39] and $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5)_2$ (51.4°),[45] indicating that a simple variation of ligand has a significant effect on the molecular structure. The dihedral angle between Ph1 of one molecule and Ph1* of a neighbouring one is 5.89°, and the dihedral angle between Ph2 and Ph2* is 9.81° (where Ph1 and Ph1* represent the centroids of phenyl ring C2–C7, and Ph2 and Ph2* represent the centroids of phenyl ring C9–C14). The corresponding Ph1 $\cdots$ Ph2* distance is 3.547 Å and Ph1 $\cdots$ Ph1* distance is 3.604 Å,[41,42] indicating that weak π–π stacking interactions exist in complex **II**. The last substructure is C–H $\cdots$ π interactions; the adjacent pairs of 5-nitrosalicylate titanocene are tied by another intermolecular C–H $\cdots$ π hydrogen bonds C14–H14 $\cdots$ Ph2 (3.602 Å) and C14–H14 $\cdots$ Ph2* (3.602 Å)[43] (Fig. 8). A three-dimensional supramolecular network structure is therefore strongly stabilized by complicated hydrogen bonds, π–π stacking and C–H $\cdots$ π interactions.

Structure comparison

The crystal structure parameters of **I** and **II** are shown in Table 3. Complex **I** crystallized in the monoclinic system

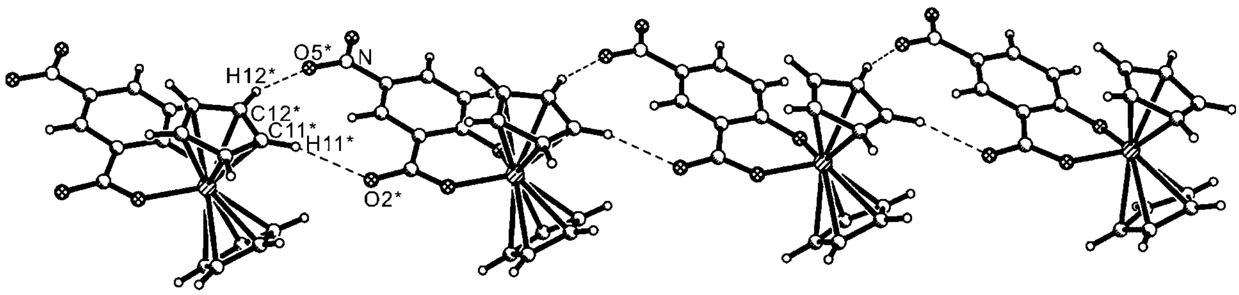


Figure 2. Intermolecular hydrogen bonding of **I**. The linear chains are assembled via hydrogen bonds along the *a*-axis. Symmetry code: $^*x, y-1, z$.

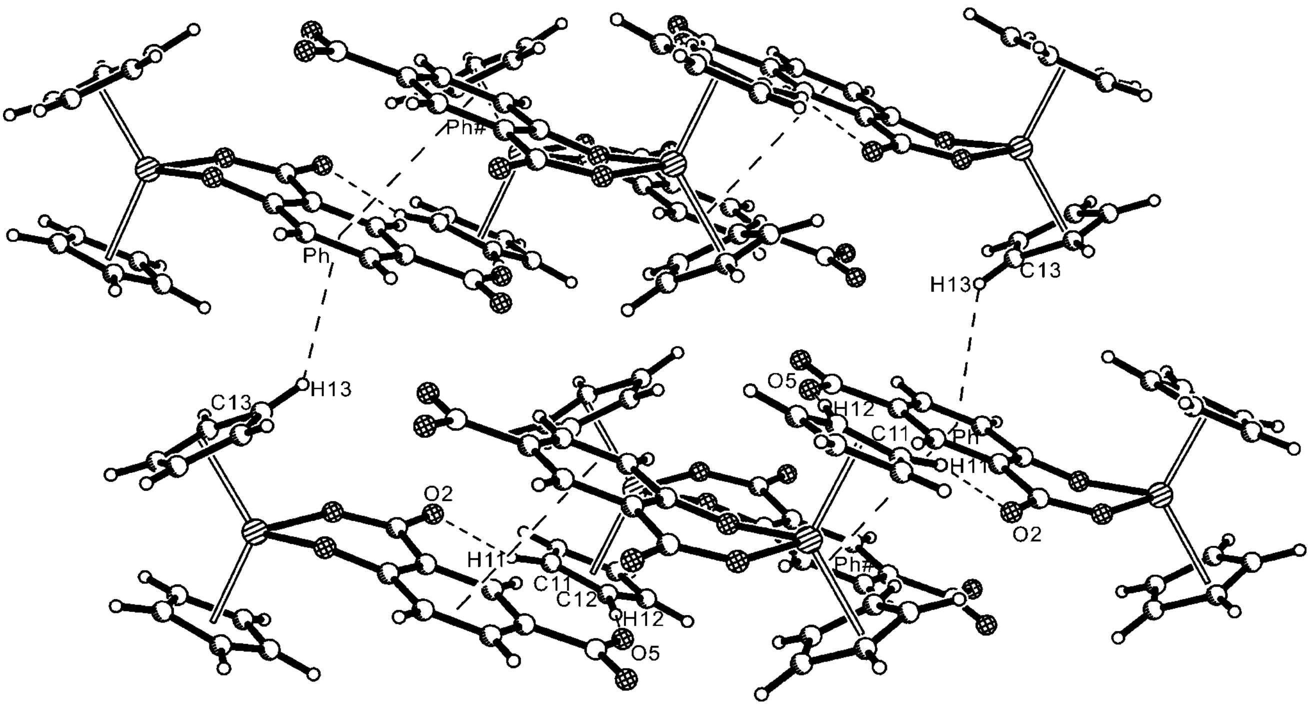


Figure 3. The double linear chains via hydrogen bonds and $\pi-\pi$ stacking formed a two-dimensional structure. A three-dimensional network structure assembled by the double layer via C–H $\cdots\pi$ interactions along the *a*-axis.

with space group $P2_1/c$, while complex **II** crystallized in the orthorhombic system with space group Pbcn. The bis(cyclopentadienyl)titanium fragments each have typically bent sandwich geometries; the dihedral angles between the planes of the C_5 rings in sandwich moieties are 50.31 and 49.37°. The titanium atom in **II** has a pseudotetrahedral coordination environment as well as in **I**. In each of the complexes, the distance between the Ti atom and Cp1 is a little different from the distance between the Ti atom and Cp2. The titanium atoms exist in the forms of mononuclear and the coordinate numbers are 4. The coordinate atoms are different.

In complex **I**, the O–Ti–O angle is 87.34°, somewhat smaller than that of $Cp_2Ti(O_2CC_6H_4O\text{-}2)$[O–Ti–O = 88.3(2)°],[49] $[Cp_2Ti(OOCCF_3)]_2(\mu\text{-}O)$ [O–Ti–O = 89.7(2)°][50] and $Cp_2Ti(O_2CCH_2CN)_2$ [O–Ti–O = 89.3(2)°],[51] but larger than that of $Cp_2Ti(C_2O_4)$ [O–Ti–O = 79.4°].[44] In complex **II**, The O–Ti–O angle is 95.80°, larger than that of $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5\text{-}2\text{-}OH)_2$ [O–Ti–O = 90.1(1)°],[39] $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5)_2$ [O–Ti–O = 91.4(3)°][45] and $Cp_2Ti(OCOCF_3)_2$ [O1–Ti–O3 = 90.14(7)°].[46] However, such a change in the O–Ti–O angle has no significant effect on the Cp1–Ti–Cp2 angle; the Cp1-Ti-Cp2 angles of complexes **I** and **II** are 132.05 and 131.93°, the values being 133.6, 133.3, 131.5, 133.3, 131.6, 131.7(5) and 132.0(1)° for $Cp_2Ti(O_2CC_6H_4O\text{-}2)$, $[Cp_2Ti(OOCCF_3)]_2(\mu\text{-}O)$, $[Cp_2Ti(O_2CCH_2CN)_2]$, $Cp_2Ti(C_2O_4)$, $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5\text{-}2\text{-}OH)_2$, $(\eta^5\text{-}C_5H_5)_2Ti(O_2CC_6H_5)_2$ and $Cp_2Ti(OCOCF_3)_2$, respectively.[39,44–46,49–51] From the unit cell of complexes **I** and **II**, it is clear that the interactions of hydrogen bonds

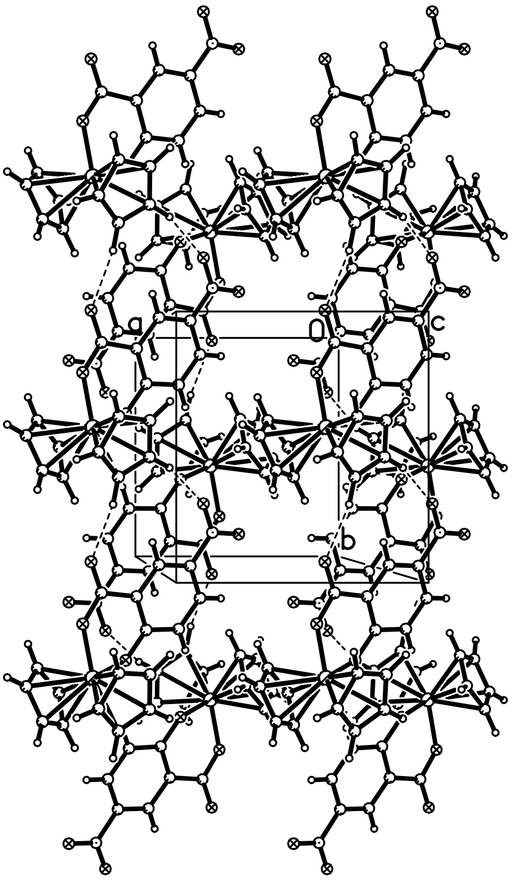


Figure 4. Projection of the unit cell of complex **I** in the [001] direction.

together with $\pi-\pi$ stacking and C–H$\cdots\pi$ interactions in the two compounds link the adjacent sheets to assemble three-dimensional network structures. The results show that, although the same ligand is used, the change of condition has great effect on the molecular structure of 5-nitrosalicylate titanocene, thereby significantly influence the weak interactions as well as the specific framework structure that forms.

EXPERIMENTAL SECTION

Materials and measurements

IR spectra were recorded as KBr pellets on an FT-IR450 spectrometer. The ^{1}H NMR spectra were recorded on an AC-80 with TMS as internal standard and DMSO-d$_6$ as solvent. Elemental analyses were determined using a PE-2400 elemental analyzer. All chemicals were of analytical reagent grade, acetyl acetone, substituted salicylic acid and Cp_2TiCl_2 used directly without further purification. Dichloromethane and hexane were dried before use.

Syntheses of complex I

Cp_2TiCl_2 (2.0 mmol) and acetyl acetone (2.0 mmol) were dissolved in 40 ml water and the mixture was stirred at room temperature for 2 h to give a deep red solution. This was added to a solution of 5-nitrosalicylate (2.2 mmol) in 30 ml NaOH solution (pH = 6.0–7.0) at 0 °C. The reaction mixture was allowed to 0 °C and stirred for 1 h to give a deep red precipitate. The reaction mixture was filtered and the precipitate was filtered and washed with HCl and H_2O, then dried under vacuum and recrystallized from dichloromethane–hexane to give **I** (86% yield) as a deep red crystalline solid; m.p. 230–232 °C, ^{1}H NMR (80 MHz, DMSO-d$_6$) δ 6.63 (s, 10H, 2 × C_5H_5), 6.83 (d, H, ArH), 8.21 (q, 1H, ArH), 8.76 (d, 1H, ArH); IR (KBr) ν: 3099, 1620, 1566, 1427, 1314, 1020, 830 cm^{-1}. Anal. calcd for $C_{17}H_{12}N_2O_7Ti$: C 56.85, H 3.65, N 3.90; found C 56.50, H 3.71, N 3.30%.

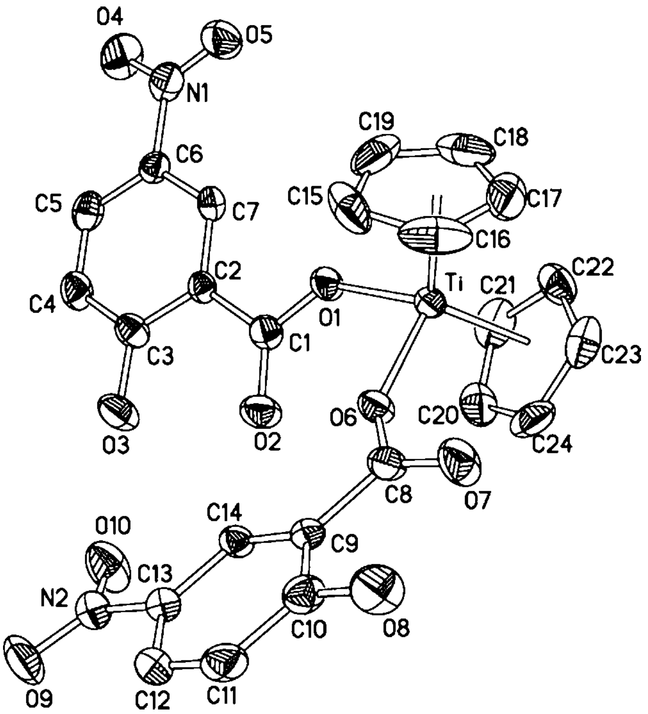


Figure 5. Molecular structure of complex **II** in the crystal with thermal ellipsoids at 30% probability; hydrogen atoms are omitted for clarity.

Syntheses of complex II

Cp_2TiCl_2 (2.0 mmol) and acetyl acetone (2.0 mmol) were dissolved in 40 ml water and the mixture was stirred at room temperature for 2 h to give a deep red solution. This was added to a solution of 5-nitrosalicylate (4.4 mmol) in 30 ml of NaOH solution (pH = 3.0–4.0) at 0 °C. The reaction mixture was allowed to 0 °C and stirred for 2 h to give an orange precipitate. The reaction mixture was filtered and the precipitate was filtered and washed with HCl and H_2O, then dried under vacuum and recrystallized from dichloromethane–hexane to give **II** (71% yield) as an orange crystalline solid; m.p. 194–195 °C, ^{1}H NMR (80 MHz, DMSO-d$_6$) δ6.68 (s, 10H, 2 × C_5H_5), 6.86 (d, 1H, ArH), 7.18 (d, 1H, ArH) 8.22 (q, 1H, ArH), 8.40 (q, 1H, ArH), 8.74 (d, 1H, ArH), 8.92 (d, 1H,

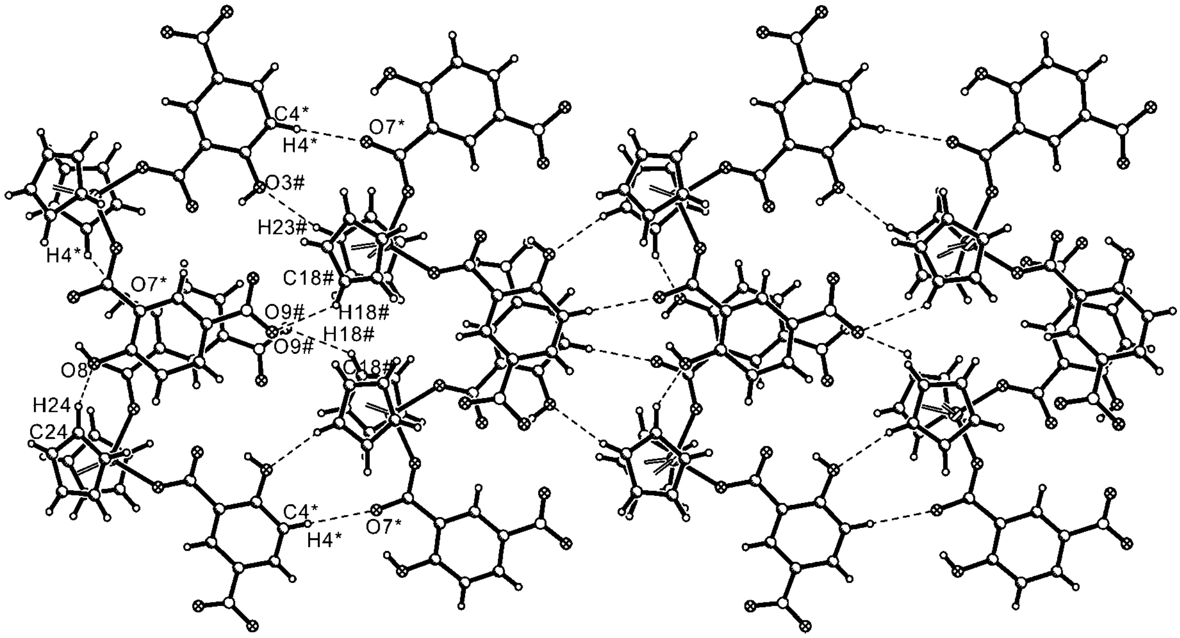


Figure 6. Part intermolecular hydrogen bonding of **II**. A network layer assembled via three intermolecular hydrogen bonds along the *c*-axis. Intramolecular hydrogen bonds O3–H3 · · · O2, O8–H8 · · · O7, C14–H14 · · · O2 and C16–H16 · · · O7 of crystallization have been omitted for clarity. Symmetry code: *1/2 − *x*, *y* − 1/2, *z*; #1/2 − *x*, 1/2 + *y*, *z*.

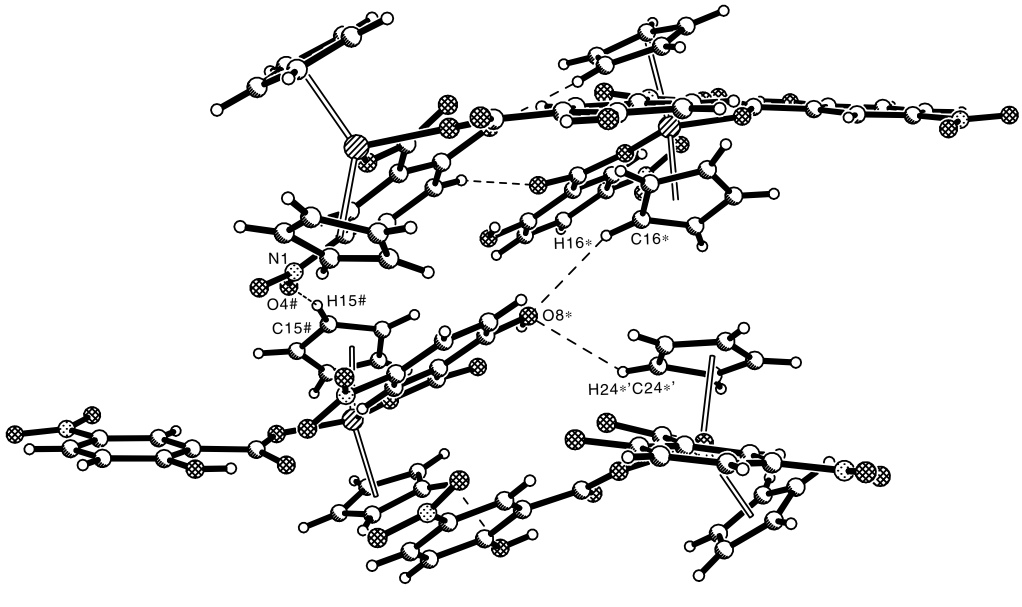


Figure 7. Part intermolecular hydrogen bonding of **II**. Symmetry code: *1 − *x*, 1 − *y*, 1 − *z*; *′1 − *x*, *y*, 1/2 − *z*; #1/2 + *x*, 1/2 − *y*, 1 − *z*.

ArH), 12.65 (s, 2H, 2 × ArOH); IR (KBr) ν: 3120, 1640, 1429, 1301, 1018, 828 cm^{-1}. Anal. calcd for $C_{24}H_{18}N_2O_{10}Ti$: C 53.15, H 3.35, N 5.17; found C 53.35, H 3.32, N 4.97%.

X-ray diffraction analysis of complexes I and II

Crystals of the complexes studied were obtained by slow diffusion of hexane into a saturated dichloromethane solution at low temperature for a month. The complexes were needle-like crystals and remarkably stable when exposed to air. The needle-like crystal of the complexes were placed into a glass capillary and sealed off. The X-ray data were collected at 298(2) K on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct method and refined on F^2 by full matrix least-squares with Bruker's SHELXL-97[52] program. All non-hydrogen atoms were refined using anisotropic thermal parameters by full matrix least-squares calculations on F^2 using the program

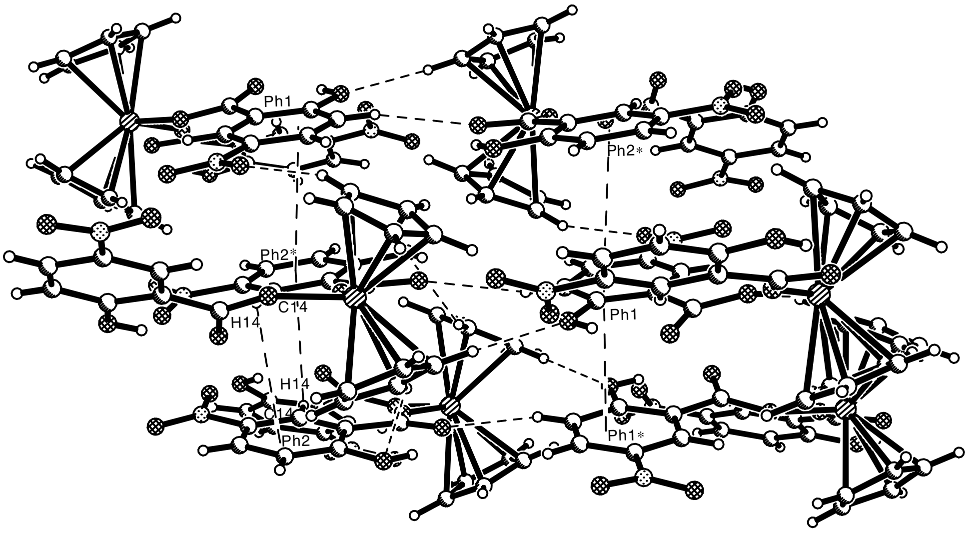


Figure 8. Part of the crystal structure of **II**. A three-dimensional network structure strongly stabilized by complicated intermolecular hydrogen bonds, $\pi-\pi$ stacking and C–H $\cdots\pi$ interactions along the *a*-axis.

Table 3. Crystallographic data for complexes **I** and **II**

	I	II
Molecular formula	$C_{17}H_{13}NO_5Ti$	$C_{24}H_{18}N_2O_{10}Ti$
Formula weight	359.18	542.30
Temperature	298(2)	298(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	Pbcn
a (Å)	8.176(14)	15.140(10)
b (Å)	8.804(15)	20.536(13)
c (Å)	20.98(4)	14.740(10)
α (deg)	90	90
β (deg)	96.43(3)	90
γ (deg)	90	90
V (Å^3)	1501(4)	4583(5)
Z	4	8
D_{calcd} (g cm^{-3})	1.590	1.572
μ (mm^{-1})	0.599	0.438
$F(000)$	736	2224
Crystal dimensions (mm)	0.43 × 0.34 × 0.08	0.27 × 0.18 × 0.13
2θ (deg)	1.95–25.08	1.98–25.05
Limiting indices	$-9 \leq h \leq 9$	$-18 \leq h \leq 14$
	$-10 \leq k \leq 5$	$-24 \leq k \leq 24$
	$-24 \leq l \leq 24$	$-17 \leq l \leq 17$
Completeness to θ	99.4% ($\theta = 25.08°$)	99.9% ($\theta = 25.05°$)
Absorption correction	Semi-empirical from equivalents	
Goodness-of-fit on F^2	1.000	1.006
Total/unique/R_{int}	5199/2647/0.0505	22762/4053/0.0910
R_1/wR_2	0.0495/0.0933	0.0475/0.0580
Peak and hole (e Å^{-3})	0.315 and −0.368	0.451 and −0.358

SHELXL-97.[53] All hydrogen atoms were treated using a riding mode. The crystals used for the diffraction study showed no decomposition during data collection.

Supplementary materials

Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 266064 and 266065 for complexes **I** and **II**, respectively. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgments

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