

Chemistry of *o*-Mercaptophenolate: Syntheses, Structures, and Characterization of Titanium(IV) Complexes

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The reaction of Cp_2TiCl_2 with *o*-mercaptophenolate in the presence of a base (Et_3N or NaOMe) afforded the complex $(BnMe_3N)_2[Ti(o\text{-}SC_6H_4O)_3]$ or $(Et_4N)_2[Ti_2(o\text{-}SC_6H_4O)_4(OMe)_2]\cdot 2H_2O$ under slightly varied conditions. Single-crystal X-ray diffraction studies showed that the Ti(IV) geometry in both complexes is a severely distorted octahedron with average *trans*-angles of 162.2° and 159.1(2)°, respectively. Crystallographic data for $(BnMe_3N)_2[Ti(o\text{-}SC_6H_4O)_3]$: $a = 9.884(3)$, $b = 16.501(7)$, $c = 23.028(7)$ Å; $\beta = 99.89(3)°$, $V = 3700.2(22)$ Å^3, $Z = 4$, final $R = 0.050$ for 3134 observed reflections; for $(Et_4N)_2[Ti_2(o\text{-}SC_6H_4O)_4(OMe)_2]\cdot 2H_2O$: $a = 8.953(4)$, $b = 10.148(3)$, $c = 14.527(3)$ Å; $\alpha = 73.16(2)°$, $\beta = 73.00(3)°$, $\gamma = 83.56(4)°$, $V = 1207.4(9)$ Å^3, $Z = 1$, final $R = 0.082$ for 2233 observed reflections. The isolation of $(BnMe_3N)_2[Ti(o\text{-}SC_6H_4O)_3]$ provides strong evidence for the synthon character of $[Ti(mp)_3]^{2-}$, which was previously predicted to be present in the complex $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$. Both electronic and ^{1}H NMR spectra showed a similar rigidity of the mp chelate rings to Ti(IV) in the complexes.

Transition metal thiolates have been extensively studied due to their relevance to biological systems[1] as well as to catalysis.[2] However, titanium thiolates have been investigated mostly for potential applications as antitumor agents,[3] nonlinear optical devices,[4] and polymer materials,[5] and in chemical sensor technology.[6] Thiotitanium or oxotitanium complexes were reported long ago[7—10] or even recently,[11,12] in which the titanium thiolates are mostly thiotitanocenes[7] or dithiotitanocenes,[6,13,14] compounds containing simultaneous O and S donor atoms at the 1,2-positions are rare. We have reported the first crystallographically characterized *o*-mercaptophenol (H_2mp) chelated titanium(IV) complex $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$[15] **3** recently. Its formation can be visualized as construction from two building blocks $[Ti(mp)_3]^{2-}$ bridged by two sodium ions through the μ_2- and μ_3-oxo atoms. At that time we were unable to obtain a pure crystalline form of the mononuclear $[Ti(mp)_3]^{2-}$ to measure the crystal structure in order to identify its presence, although its tetraethylammonium salt was characterized spectroscopically twenty years ago.[16] This paper reports on the crystal structure of $(BnMe_3N)_2[Ti(mp)_3]$ **1** as well as a dimeric complex **2** by a variation of the reaction conditions.

Experimental

All operations were carried out under a dinitrogen atmosphere with a Schlenk-type apparatus. Solvents were dried over molecular sieves and degassed before use. $TiCl_4$ (Beijing), cyclopentadiene (HCp, Merck–Schuchardt), *o*-mercaptophenol (H_2mp, Merck–Schuchardt) and $BnMe_3NBr$ (Bn = benzyl) were used as received. Cp_2TiCl_2 was prepared according to a literature method.[17]

Infrared spectra were obtained from a Perkin–Elmer 577 spectrophotometer in the range 4000—300 cm^{-1} in KBr pellets. The electronic spectra were recorded on a Shimadzu UV-3000 spectrophotometer in DMF solutions. ^{1}H NMR spectra were measured on a Varian Unity 500 spectrometer in DMSO-d_6 with TMS internal standard and downfield from it as positive. Elemental analyses were carried out by the Analytical Chemistry Division of Fujian Institute.

1) Preparation of Complexes. **a) $(C_6H_5CH_2Me_3N)_2[Ti(o\text{-}SC_6H_4O)_3]$ (1).** To a slurry of Cp_2TiCl_2 (0.22 g, 1.0 mmol) in MeCN (10 cm^3) was added a solution of H_2mp (0.30 cm^3, 3.0 mmol) and Et_3N (0.84 cm^3, 6.0 mmol) in MeCN (5.0 cm^3) under stirring at room temperature. The reaction solution was filtered after stirring for 20 h, and was added to a MeOH solution (15 cm^3) of $BnMe_3NBr$ (0.46 g, 2.0 mmol). Brownish-red crystals of **1** were obtained after the solution had been kept at 4 °C for two weeks. The microcrystalline product was recrystallized from 1 : 1 DMF/MeOH (10 cm^3) to give 0.35 g of rod-like reddish-brown crystals of complex **1**. (yield 50%). Found: C, 63.04; H, 6.01; N, 3.97; S, 13.68; Ti, 6.21%. Calcd for $C_{38}H_{44}N_2O_3S_3Ti$: C, 63.32; H, 6.15; N, 3.89; S, 13.34; Ti, 6.64%. IR (KBr) 3051w, 3031w, 3012w, 2980w, 2955w, 1561w, 1484m, 1450s, 1433s, 1284s, 1232s, 1110m, 1065m, 1023m, 889m, 849s, 753s, 724s, 704m, 687s, 616s, 544m, 437s, 365s, 303m cm^{-1}. UV λ_{max} (DMF, nm) 315 (ε 27000 M^{-1} cm^{-1}), 415 (9000 M^{-1} cm^{-1}). ^{1}H NMR (DMSO-d_6) the cations: δ = 2.993 (CH_3, 18H), 4.490 (CH_2, 4H), 7.525 (C_6H_5, 10H); the phenyl rings: δ = 6.127—6.712 (see Table 4 for explanation).

b) $(Et_4N)_2[Ti_2(o\text{-}SC_6H_4O)_4(OMe)_2]\cdot 2H_2O$ (2). To a MeOH (30 cm^3) solution containing Cp_2TiCl_2 (0.43 g, 2.0 mmol) and

NaOMe (0.43 g, 8.0 mmol) was added H_2mp (0.41 cm^3, 4.0 mmol) with stirring; the reaction mixture turned brownish red immediately. The reaction solution was filtered after stirring at room temperature for 5 h, and to the filtrate was added Et_4NCl (0.66 g, 4.0 mmol) in MeOH (10 cm^3) to give a medium amount of precipitates. The reaction mixture was filtered again and compound $(Et_4N)_2[Ti(o\text{-}SC_6H_4O)_3Na(MeOH)_2]_2$ **3** was obtained from the filtrate (yield ca. 10%), which was identified as being the same as that reported.[15] The precipitate was dissolved in a suitable amount of MeCN (30 cm^3) and filtered. This brownish-red filtrate was added to MeOH (10 cm^3) and kept at 4 °C to give dark-brown square crystals of **2**. Yield, 35%. Found: C, 52.88; H, 6.45; N, 2.87; S, 14.17; Ti, 9.34%. Calcd for $C_{42}H_{66}N_2O_8S_4Ti_2$: C, 53.04; H, 6.99; N, 2.94; S, 13.48; Ti, 10.07%. Selected IR (KBr) 3400br, 3047w, 2982w, 2918w, 1568w, 1451vs, 1264vs, 1234s, 1022s, 866s, 750s, 691s, 627s, 552m, 493s,br, 441s, 406w, 382m, 368m cm^{-1}. UV λ_{max} (DMF, nm) 305 (ε 40000 M^{-1} cm^{-1}), 415 (11000 M^{-1} cm^{-1}). ^{1}H NMR (DMSO-d_6) the cations: δ = 1.144 (t, CH_3, 24H), 3.186 (q, CH_2, 16H); the bridges: δ = 3.172 (s, OCH_3, 6H); the phenyl rings: δ = 6.129—6.707 (see Table 4 for explanation).

2) X-Ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. Single crystals of suitable sizes were mounted on glass fibers with epoxy resin and diffraction data were collected on diffractometers, as described in Table 1. Crystallographic data for both complexes **1** and **2** are also summarized in the Table 1. The light source was Mo $K\alpha$ radiation (λ = 0.71073 Å) monochromated by graphite using the ω–2θ scan mode. The reflections were corrected for anisotropic decay and Lorentz-polarization effects, and an empirical absorption correc-

Table 2. Selected Atomic Distances (Å) and Bond Angles (°) for $(C_6H_5CH_2Me_3N)_2[Ti(o\text{-}SC_6H_4O)_3]$ (**1**)

Ti–O(1)	1.950(4)	Ti–S(1)	2.437(2)
Ti–O(2)	1.910(5)	Ti–S(2)	2.459(2)
Ti–O(3)	1.921(4)	Ti–S(3)	2.469(2)
C(11)–O(1)	1.346(8)	C(16)–S(1)	1.742(7)
C(21)–O(2)	1.334(8)	C(26)–S(2)	1.774(9)
C(31)–O(3)	1.345(8)	C(36)–S(3)	1.761(8)
O(1)–Ti–S(1)	79.81(14)	O(1)–Ti–S(3)	162.26(14)
O(2)–Ti–S(2)	79.2(2)	O(2)–Ti–S(1)	164.3(2)
O(3)–Ti–S(3)	80.08(13)	O(3)–Ti–S(2)	160.07(14)
O(1)–Ti–O(2)	94.0(2)	S(1)–Ti–S(2)	87.65(9)
O(2)–Ti–O(3)	92.8(2)	S(2)–Ti–S(3)	84.11(8)
O(1)–Ti–O(3)	98.3(2)	S(1)–Ti–S(3)	83.27(8)
O(1)–Ti–S(2)	100.41(15)	C(11)–O(1)–Ti	125.5(4)
O(2)–Ti–S(3)	103.74(15)	C(21)–O(2)–Ti	129.5(5)
O(3)–Ti–S(1)	102.37(15)	C(31)–O(3)–Ti	127.1(4)
C(16)–S(1)–Ti	98.8(3)		
C(26)–S(2)–Ti	96.6(3)		
C(36)–S(3)–Ti	97.1(2)		

Table 1. Crystallographic Data for $(C_6H_5CH_2Me_3N)_2[Ti(o\text{-}SC_6H_4O)_3]$ (**1**) and $(Et_4N)_2[Ti_2(o\text{-}SC_6H_4O)_4(OMe)_2]\cdot 2H_2O$ (**2**)

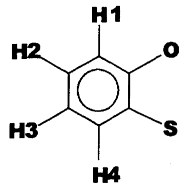
Complex	**1**	**2**
Empirical formula	$C_{38}H_{44}N_2O_3S_3Ti$	$C_{42}H_{66}N_2O_8S_4Ti_2$
Fw	720.83	951.06
Color and habit	Dark-brown block	Reddish brown prism
Diffractometer	Siemens SMART CCD	Enraf-Nonius CAD4
2θ range/°	46.5	50
Temp/K	293 ± 1	296 ± 1
Space group	Cc	$P\bar{1}$
Crystal dimensions/ mm^3	$0.5\times0.25\times0.25$	$0.38\times0.25\times0.10$
Crystal system	Monoclinic	Triclinic
a/Å	9.884(3)	8.953(4)
b/Å	16.501(7)	10.148(3)
c/Å	23.028(7)	14.527(3)
α/°		73.16(2)
β/°	99.89(3)	73.00(3)
γ/°		83.56(4)
V/Å^3	3700.2(22)	1207.4
Z	4	1
ρ/g cm^{-3}	1.294	1.31
μ/mm^{-1}	0.439	0.54
F(000)	1520	504
Reflections collected	3521	4243
No. of obsd reflns	3134 ($I>2\sigma(I)$)	2233 ($I>2.5\sigma(I)$)
No. of variables	314	301
R_1/%[a]	5.05	8.2
R_2/%	12.35[b]	8.6[c]
Goodness of fit	1.053	0.87
Highest residual peak/e Å^3	0.419	0.93
Lowest residual peak/e Å^3	−0.269	−0.16

a) $R_1=\sum||F_o|-|F_c||/\sum|F_o|$.
b) $R_2=R_w=[\sum w(|F_o^2|-|F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$; $w=1/[\sigma^2|F_o^2|+(0.056P)^2+10.239P]$, where $P=[|F_o^2|+2|F_c^2|]/3$. c) $R_2=R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w=1/[\sigma^2|F_o^2|+(0.01F_o)^2+1.0]$.

Table 3. Selected Atomic Distances (Å) and Bond Angles (°) for $(Et_4N)_2[Ti_2(o\text{-}SC_6H_4O)_4(OMe)_2]\cdot 2H_2O$ (**2**)

Ti–S(1)	2.421(3)	Ti–S(2)	2.436(4)
Ti–O(1)	1.960(8)	Ti–O(2)	1.964(8)
Ti–O(3)	1.996(7)	Ti–O(3a)	2.009(6)
C(16)–S(1)	1.73(1)	C(11)–O(1)	1.35(1)
C(26)–S(1)	1.73(2)	C(21)–O(2)	1.38(1)
C(3)–O(3)	1.41(1)	Ti···Ti(a)	3.214(3)
S(1)–Ti–O(1)	80.7(2)	S(1)–Ti–O(2)	106.1(2)
S(2)–Ti–O(2)	81.9(2)	S(1)–Ti–O(3)	92.7(2)
S(1)–Ti–S(2)	82.7(1)	S(1)–Ti–O(3a)	158.6(3)
O(1)–Ti–O(2)	90.5(3)	S(2)–Ti–O(1)	159.1(2)
O(1)–Ti–O(3)	109.7(3)	S(2)–Ti–O(3)	83.7(2)
O(1)–Ti–O(3a)	88.7(3)	S(2)–Ti–O(3a)	111.0(3)
O(2)–Ti–O(3)	154.6(3)	O(3)–Ti–O(3a)	73.3(3)
Ti–S(1)–C(16)	97.8(4)	O(2)–Ti–O(3a)	92.5(3)
Ti–S(2)–C(26)	96.6(4)	Ti–O(1)–C(11)	124.3(7)
Ti–O(3)–C(3)	129.2(6)	Ti–O(2)–C(21)	122.0(7)

Table 4. Comparison of Chemical Shifts of Protons on the o-Mercaptophenolate Rings of Complexes **1**—**3**



Proton	Chemical shift/ppm		
	1	**2**	**3**
1	6.142	6.136	6.138
2	6.525	6.523	6.524
3	6.333	6.332	6.330
4	6.700	6.703	6.698

tion based on a series of psi-scans was applied to the data. The structures were solved by direct methods on a COMPAQ computer either with the Siemens SHELXTL (complex **1**) or the MolEN/PC[18] (complex **2**) program package,[19] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen-atom positions (idealized) were added to the structure factor calculations isotropically and were not refined. Tables of positional parameters, complete atomic distances and bond angles, and structure factors are deposited as Document No. 71047 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Synthesis. The reaction of Cp_2TiCl_2 with mp^{2-} in acetonitrile in a ratio of 1 : 3 gave a mononuclear species $[Ti(mp)_3]^{2-}$ which was precipitated by adding the counter ion $BnMe_3N^+$ to give complex $(BnMe_3N)_2[Ti(mp)_3]$ (**1**). If the reaction was run in a ratio of 1 : 2 in methanol in the presence of NaOMe instead of Et_3N, complex $(Et_4N)_2[Ti_2(mp)_4(OMe)_2]\cdot 2H_2O$ (**2**) was isolated by recrystallization of the precipitates from MeCN : MeOH (3 : 1 v : v) upon the addition of Et_4NCl to the reaction solution. The water molecules might have been introduced either during recrystallization (due to the humid weather of southern China) or from the solvents. In the same reaction system, complex $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$ (**3**) could be obtained from the filtrate. The reaction pathways can be seen from Scheme 1 shown below, where the dotted brackets indicate the speculated species. It is noted that during the reaction processes, the species $Ti(mp)_2$ could have formed first when the amount of mp^{2-} is limited. It would quickly transform either into the six-coordinate $[Ti(mp)_3]^{2-}$ in the presence of more mp^{2-}, which is the "synthon" in further reactions and can be considered as the building block just as in the case of vanadium,[20—22] or into the dimeric complex **2** in the presence of an excess of MeO^- as bridging groups.

Structures. The selected atomic distances and bond angles for complexes **1** and **2** are listed in Tables 2 and 3, respectively. Both complexes consist of discrete cations and anions, and the asymmetric unit contains one anion and two cations, while **2** also contains two solvated water molecules.

The molecular structure of the anions of **1** is shown in Fig. 1. The chiral anion of **1** contains a titanium atom unsymmetrically coordinated by three oxygen and three sulfur atoms from three mp^{2-} ligands in a facial configuration with dihedral angles of the least-squares planes of the chelate rings average to 77.8°. The average *trans*-angles O–Ti–S of 162.2° is very close to that found for its vanadium-analogue (average 162.5°).[23] Thus, the geometry of Ti(IV) in this complex could best be described as a distorted octahedron, since the *trans*-angles should be 180° for an idealized octahedron, and a 1,2-bidentate ligand forming a five-membered chelate ring could reduce that angle to 173°. The average bite angle is 79.7°, very similar to the Mo(V) analogue.[24] The Ti–S distances (average 2.455 Å) are slightly longer than those in complex **3** (average 2.429 Å).[15]

The centrosymmetric anionic structure of complex **2** is shown in Fig. 2. It is a dimer of structural unit $[Ti(mp)_2(OMe)]^-$, connected via the methoxy bridges by

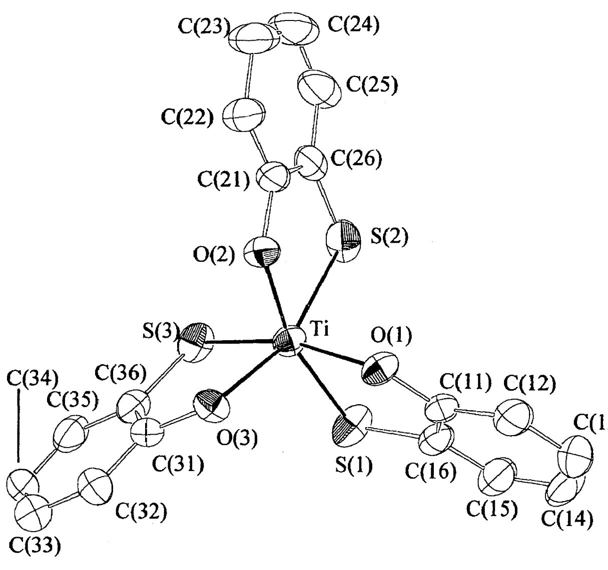
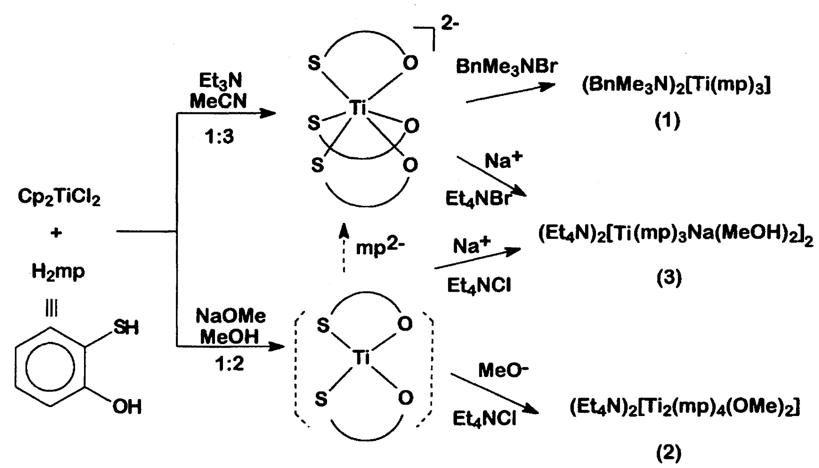


Fig. 1. ORTEP structure of anion of complex $(C_6H_5CH_2Me_3N)_2[Ti(o\text{-}SC_6H_4O)_3]$ (**1**) in 40% probability ellipsoids.



Scheme 1. Reaction pathways for the formation of complexes **1**—**3**.

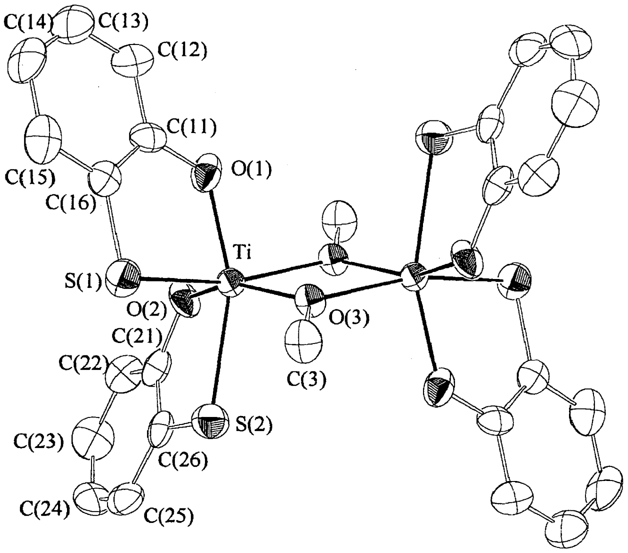


Fig. 2. ORTEP structure of anion of complex $(Et_4N)_2[Ti_2(o\text{-}SC_6H_4O)_4(OMe)_2]\cdot 2H_2O$ (**2**) in 40% probability ellipsoids.

two nearly equivalent Ti–O bonds with Ti···Ti distance of 3.214(3) Å, slightly shorter than those in complexes $Ti_2Cl_4(\mu\text{-}OPh)_2(OPh)_2$ (3.274(3) Å)[10] and $[Ti(\mu\text{-}OPh)(OPh)_3(HOPh)]_2$ (3.309(5) Å).[9a] The rhombic unit Ti_2O_2 is planar with Ti–O(3)–Ti and O(3)–Ti–O(3a) angles being 106.7(3)° and 73.3(3)°, respectively. Each Ti(IV) ion can be considered as a greatly distorted octahedron and assuming O(1) and S(2) the axial atoms (O(1)–Ti–S(2) 159.1(2)°), the equatorial plane would be composed of S(1), O(2), O(3a), and O(3). The two mp^{2-} ligands are both terminally coordinated to Ti and form five-membered chelate rings, where the least-squares planes of the two rings form a dihedral angle of 77°, while each then forms an angle of 70.2° and 66.9° with the Ti_2O_2 plane, respectively. The $Ti–O_{mp}$ bonds (average 1.962 Å) are relatively long compared to that in complex **1** or **3**, while the $Ti–O_{OMe}$ bonds are the longest (average 2.003±0.006 Å) in the molecule. Such long $Ti–O_{OR}$ bonds have been observed for the bridging groups in $Ti_2Cl_4(\mu\text{-}OPh)_2(OPh)_2$ (average 2.016 Å)[10] and $[Ti(\mu\text{-}OPh)(OPh)_3(HOPh)]_2$ (average 2.036 Å).[9a] The Ti–S bonds are shortened due to a *trans*-effect caused by the relatively long Ti–O bonds, and are very close to that found in **3** with similar values of 2.429 Å.[15] The bite angles (average 81.3°) of the mp^{2-} ligands fall in the range for other *o*-mercaptophenolate chelated complexes.[23,24] In both complexes **1** and **2**, the chelate angles Ti–S–C and Ti–O–C are as usually reported[22] and nearly in the same range of 97.5±0.2° and 125±2°, respectively. One of the two solvated water molecules in **2** forms a weak hydrogen bond with the O(2) atom with an $O(2)\cdots O_w(4)$ distance of 2.86 Å.

The shapes of the electronic absorption spectra of complexes **1** and **2** in DMF are very similar and both showed two maxima. The similarity in the two spectra is an indication of the presence of similar active chromophores in dilute DMF solutions. That at 415 nm in both complexes belongs to an LMCT transition. The band at 305 nm for **2** is hypsochromically shifted by 10 nm compared to that for **1**, and possibly caused in both cases by L–L transitions (π–π) in the mp ligands. The 10 nm blue shift might be an indication of a different arrangement of the chelates to Ti(IV).

A comparison of the chemical shifts of ^1H NMR in DMSO-d_6 of the protons on the *o*-mercaptophenolate ligands in complexes **2** and **3** (Table 4) with that of complex **1** showed that these ligands are quite similarly coordinated to Ti(IV), and not much influenced by dimerization through the MeO^- bridges, as in **2**, or by further ligations of the oxygen atoms to form μ_2- or μ_3-O bridges, as in **3**. This phenomenon is a strong indication of the rigid chelating character of mp^{2-} to Ti, and also implies the integrity of the structural unit $[Ti(mp)_3]^{2-}$; its basic skeleton is maintained when functioning as a synthon to form dimeric complex **3**. The fact that the protons on the mercaptophenolate rings in all three complexes showed only one set of peaks in ratio of 1 : 1 : 1 : 1 as d : t : t : d (d for doublet, t for triplet), respectively, also illustrates that all mp ligands in the complexes are equivalent.

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