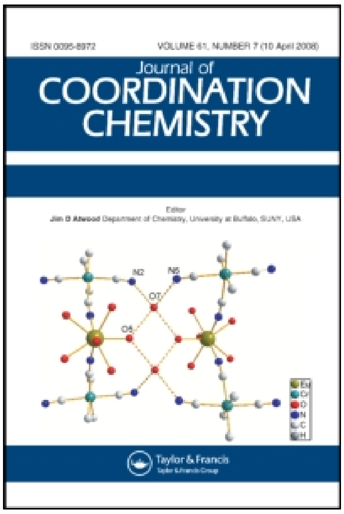

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A TITANIUM(IV) DIMER COMPLEX CONTAINING TRLS(2-MERCAPTOPHENOLATO)TITANIUM(IV) FRAGMENTS LINKED BY SODIUM IONS. SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$ (H_2mp = 2-MERCAPTOPHENOL)

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To cite this Article Wen, Ting-Bin , Wu, Da-Xu , Shi, Ji-Cheng , Chen, Chang-Neng , Liu, Qui-Tian and Kang, Bei-Sheng(1997) 'A TITANIUM(IV) DIMER COMPLEX CONTAINING TRLS(2-MERCAPTOPHENOLATO)TITANIUM(IV) FRAGMENTS LINKED BY SODIUM IONS. SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$ (H_2mp = 2-MERCAPTOPHENOL)', Journal of Coordination Chemistry, 42: 1, 11 — 23
To link to this Article: DOI: 10.1080/00958979708045276
URL: http://dx.doi.org/10.1080/00958979708045276

J. Coord. Chem., 1997, Vol. 42, pp. 11–23
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Printed in Malaysia

A TITANIUM(IV) DIMER COMPLEX CONTAINING *TRIS*(2-MERCAPTOPHENOLATO)TITANIUM(IV) FRAGMENTS LINKED BY SODIUM IONS. SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$ (H_2mp = 2-MERCAPTOPHENOL)

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(Received 24 July 1996)

The dimeric complex $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$ (**1**) was prepared by reaction of Cp_2TiCl_2, H_2mp (H_2mp = 2-mercaptophenol) and CH_3ONa in methanol and structurally characterized by X-ray diffraction methods. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.425(6)$, $b = 17.404(4)$, $c = 18.256(7)$ Å, $\beta = 126.00(5)°$, $V = 3193.6$ Å^3, and $Z = 2$. The structure was refined to R (R_w) = 0.050 (0.064) for 3701 reflections ($I > 3\sigma(I)$). The anion contains two $[Ti(mp)_2]^{2-}$ fragments linked by sodium ions through the μ_2-O and μ_3-O bridges to form a $Ti_2Na_2O_6$ core which can be interpreted as two corner-voided oxocubane-like $TiNa_2O_4$ subunits sharing the Na_2O_2 face. The structure of the symmetric heterometallic tetranuclear $[Ti(mp)_3Na(MeOH)_2]_2^{2-}$ anion possesses a crystallographic inversion centre. Each Ti(IV) atom in a distorted octahedral coordination geometry is chelated by three mp ligands with $S_tO_{b\text{-}D}$ and $S_tO_{b\text{-}T}$ coordination modes. Complex (**1**) was also investigated by infrared, electronic, ^{1}H NMR and ^{13}C NMR spectroscopies.

Keywords: 2-mercaptophenolato; titanium; cubane; X-ray structure

INTRODUCTION

Current interest in the chemistry of transition metal thiolates has been stimulated by the pertinence of such complexes to bioinorganic systems,[1] as well as by the

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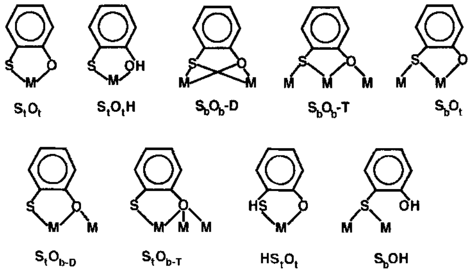
inability to act as metalloligands and thus as synthons ('building blocks') for multinuclear complexes.[2-3] Bidentate thiolates as a fundamental ligand type, have received much attention only recently[4-8] due to their multifunctional character in ligation and chelation to metal atoms. Recently we have developed broad research involving transition metal complexes with thiolato ligands such as 2-mercaptophenol (H_2mp),[8-10] 2-mercapto-3-pyridinol (H_2mpp)[11] and 2-mercaptopyridine-*N*-oxide (Hmpo).[12-13] Reactive species in the formation of these complexes and their function in the construction of cluster complexes have been reviewed.[3] Structural studies showed that H_2mp exhibits a variety of coordination modes with transition metal atoms[3,9b] (See Scheme 1).



(t for terminal, b for bridge, D for dinuclear and T for trinuclear)

SCHEME 1 Coordination modes of 2-mercaptophenol.

We now extend our studies to titanium whose thiolato complexes have been investigated for potential applications as antitumor agents,[14] non-linear optical[15] and polymer materials,[16] and in chemical sensor technology.[2c] While thiotitanium or oxotitanium complexes have been studied extensively,[2,17-19] compounds containing O and S at 1,2-positions have not been reported. Until recently, most titanium thiolato complexes reported were tianocenethiolate[17] or tianocenedithiolate[2] derivatives. To our knowledge, even structural results for *tris*(1,2dithiolato)titanium (IV) complexes are limited.[6,20] In this contribution, we report the complex $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$ (**1**), a dimer derived from the structural unit *tris* (2-mercaptophenolato)titanium(IV) $[Ti(mp)_3]^{2-}$, linked by two sodium ions.

EXPERIMENTAL

General

All operations were carried out under an atmosphere of dinitrogen using conventional Schlenk techniques. All solvents were dried over molecular sieves and degassed before use. $TiCl_4$ (Beijing), cyclopentadiene (Merck-Schuchardt), 2-mercaptophenol (H_2mp) (Merck-Schuchardt), and Et_4NCl (Aldrich) were commercially available. Cp_2TiCl_2 was prepared according to a literature method.[21]

Infrared spectra were obtained using a Perkin Elmer 577 spectrophotometer in the range 4000-300 cm^{-1}. The electronic spectrum was recorded on a Shimadzu UV-3000 spectrophotometer in DMF solution. ^1H NMR, ^{13}C NMR, ^1H-^1H COSY and ^1H-^{13}C HMQC spectra were measured on a Varian Unity 500 spectrometer in DMSO-d_6. Elemental analyses were carried out by the Analytical Chemistry Group of this Institute.

Synthesis of $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$(1)

To a suspension of Cp_2TiCl_2 (0.22 g, 1 mmol) and CH_3ONa (0.32 g, 6 mmol) in CH_3OH (40 cm^3, H_2mp (0.31 cm^3, 3 mmol, d_{20} = 1.22 g/cm^3) was added *via* a syringe. After the reaction mixture was stirred at room temperature for 5 hr and filtered, a red brown solution was obtained. Some 0.33 g of Et_4NCl (2 mmol) in 20 cm^3 of CH_3OH was added to the solution, a small amount of brown powder was removed by filtration, and the volume of the filtrate was reduced by half. Storage of the filtrate at 4°C for several days gave (**1**) as dark brown, well-formed prisms, yield 0.18 g (28%). *Anal.* Calcd. for $C_{56}H_{80}N_2Na_2O_{10}S_6Ti_2$(%): C, 52.74; H, 6.32; N, 2.20; Na, 3.60; S, 15.08; Ti, 7.51. Found: C, 52.23; H, 5.78; N, 2.39; Na, 3.74; S, 15.46; Ti, 6.97. IR (KBr): 3040 (w), 1561(w), 1542 (s), 1391(m), 1277(s), 1233(s), 1172(m), 1026(m), 843(s), 789(w), 757(s), 726(w), 687(s), 613(s), 546(w), 436(m), 373(m) cm^{-1}.

Crystal Data, Structure Determination and Refinement

Crystallographic data for (**1**) are summarized in Table I. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with MoKα radiation (λ = 0.71073 Å) and graphite monochromator using the ω-2θ scan mode. The intensities of three standard reflections were measured every 120 min, indicating a total loss in intensity of 2.3%. The reflections were corrected for anisotropic decay, Lorentz polarization and empirical absorption (Ψ scan) effects. Intensities of equivalent reflections were averaged (R_{int} = 1.7%). The structure was solved by direct methods on a COMPAQ PL4/50 computer with the MolEN/PC program package[22] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atom positions (idealised) were added to the structure factor calculations but not refined.

TABLE I Crystallographic data for (**1**)

Emperical formula	$C_{56}H_{80}N_2Na_2O_{10}S_6Ti_2$
Molecular weight	1275.43
Crystal colour, size (mm)	dark brown, 0.56 × 0.36 × 0.22
Temperature (K)	296(1)
Crystal system	monoclonic
Space group	$P2_1/c$
a(Å)	12.425 (6)
b(Å)	17.404 (4)
c(Å)	18.256 (7)
β(°)	126.00 (5)
V(Å^3)	3193.6
Z	2
D_{calc}(g cm^{-3})	1.33
μ (Mo-Kα) (cm^{-1})	5.0
2θ range (°)	2 to 50
F(000)	1344
No. of reflections measured	6066
No. of independent reflections	5831
No. of observed reflections ($I > 3\sigma(I)$)	3701
No. of parameters refined	352
R^a	0.050
$R_w{}^b$	0.064
Weight scheme	$4Fo^2/\sigma^2(Fo^2)$
Goodness of fit	1.27
Max. shift in final cycle	0.00
Final $\Delta\rho_{max}$ (e Å^{-3})	0.39

$^aR = \Sigma(|Fo| - |Fc|)/\Sigma|Fo|$, $^bR_w = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w(|Fo|^2]^{1/2}$

RESULTS AND DISCUSSION

The reaction of *bis*(cyclopentadienyl)titanium(IV) dichloride with 2-mercaptophenol and sodium methoxide and subsequent cation exchange with tetraethylammonium chloride in methanol afforded the complex $(Et_4N)_2[Ti(mp)_3Na(MeOH)_2]_2$ (**1**). This complex is quite similar to the previously reported[9b] dimeric complex $(Et_4N)_2[V(mp)_3Na(MeOH)_2]_2$ (**2**), obtained from VCl_3 directly when reacted with Na_2mp, in which the V^{3+} ion was oxidized. It is believed that reaction of Cp_2TiCl_2 with mp^{2-} produces first the reactive species $[Ti(mp)_3]^{2-}$ by a simple substitution and this further coordinates to the sodium ions present in solution *via* the oxygen donors to form the dimeric complex as was the case for the V-analogue (**2**).

The single-crystal structure of (**1**) has been solved by X-ray methods. Final positional parameters of non-hydrogen atoms are listed in Table II. Selected bond lengths and angles are given in Table III. An ORTEP view of $[Ti(mp)_3Na(MeOH)_2]_2{}^{2-}$ is depicted in Figure 1.

TABLE II Atomic coordinates and thermal parameters for(**1**)

Atom	*x/a*	*y/b*	*z/c*	B_{eq} *(Å^2)*
Ti	0.88653(6)	0.06247(4)	0.82000(4)	2.51(2)
S(1)	1.00848(9)	0.12396(7)	0.76963(6)	3.53(3)
S(2)	0.7889(1)	0.18904(7)	0.80018(6)	3.44(3)
S(3)	0.71498(9)	0.03962(7)	0.66119(6)	3.25(3)
Na	0.8410(1)	0.0030(1)	0.98070(9)	3.37(4)
O(11)	1.0180(2)	−0.0162(2)	0.8524(2)	3.03(6)
O(21)	0.9743(2)	0.0901(2)	0.9474(1)	2.68(6)
O(31)	0.7735(2)	−0.0074(2)	0.8299(1)	2.92(6)
O(1)	0.7270(3)	−0.0904(2)	1.0090(2)	4.72(9)
O(2)	0.6685(3)	0.0954(2)	0.9073(2)	5.71(9)
C(1)	0.6182(5)	−0.0592(4)	1.0039(4)	7.2(2)
C(2)	0.6218(5)	0.1550(4)	0.9316(4)	7.6(2)
C(11)	1.0864(3)	−0.0226(3)	0.8162(2)	3.1(1)
C(12)	1.1503(4)	−0.0907(3)	0.8213(3)	4.2(1)
C(13)	1.2227(4)	−0.0938(3)	0.7860(3)	5.5(1)
C(14)	1.2314(4)	−0.0301(4)	0.7456(3)	5.8(1)
C(15)	1.1679(4)	0.0375(3)	0.7387(3)	4.9(1)
C(16)	1.0932(3)	0.0415(3)	0.7732(2)	3.4(1)
C(21)	0.9667(3)	0.1596(2)	0.9782(2)	2.48(9)
C(22)	1.0350(4)	0.1748(3)	1.0697(2)	3.2(1)
C(23)	1.0209(4)	0.2450(3)	1.0988(2)	3.9(1)
C(24)	0.9407(4)	0.3015(3)	1.0357(3)	4.0(1)
C(25)	0.8744(4)	0.2876(3)	0.9456(2)	3.4(1)
C(26)	0.8840(3)	0.2160(2)	0.9147(2)	2.83(9)
C(31)	0.6628(3)	−0.0432(2)	0.7619(2)	2.9(1)
C(32)	0.5944(4)	−0.0960(3)	0.7771(3)	3.8(1)
C(33)	0.4800(4)	−0.1307(3)	0.7042(3)	4.3(1)
C(34)	0.4353(4)	−0.1128(3)	0.6181(3)	4.4(1)
C(35)	0.5009(4)	−0.0603(3)	0.6013(2)	3.7(1)
C(36)	0.6166(3)	−0.0253(2)	0.6728(2)	2.9(1)
N	0.2830(3)	0.1593(2)	0.5098(2)	4.5(1)
C(111)	0.2479(5)	0.0753(3)	0.5020(3)	5.7(2)
C(112)	0.1118(6)	0.0564(4)	0.4777(5)	9.0(3)
C(121)	0.1847(6)	0.2013(3)	0.4213(4)	6.7(2)
C(122)	0.1823(8)	0.1731(4)	0.3419(4)	9.4(3)
C(131)	0.2776(5)	0.1985(4)	0.5806(3)	6.2(1)
C(132)	0.3693(6)	0.1671(5)	0.6748(4)	8.9(2)
C(141)	0.4237(5)	0.1620(4)	0.5354(3)	6.2(1)
C(142)	0.4822(54)	0.2399(5)	0.5486(4)	9.0(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $4/3[a^2B(1,1)b + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

TABLE III Selected bond lengths (Å) and angles (°) for (**1**)

Bond lengths			
Ti—S(1)	2.434(1)	Ti—S(2)	2.437(1)
Ti—S(3)	2.417(1)	Ti—O(11)	1.939(3)
Ti—O(21)	1.962(3)	Ti—O(31)	1.945(3)
S(1)—C(16)	1.759(5)	S(2)—C(26)	1.756(4)
S(3)—C(36)	1.766(5)	Na—O(21)	2.567(3)
Na—O(31)	2.367(3)	Na—O(11′)	2.477(2)

TABLE III (*Continued*)

Bond lengths			
Na—O(21′)[a]	2.465(2)	Na—O(1)	2.404(4)
Na—O(2)	2.367(4)	O(11)—C(11)	1.352(5)
O(21)—C(21)	1.360(5)	O(31)—C(31)	1.347(5)
O(1)—C(1)	1.408(7)	O(2)—C(2)	1.381(8)
Bond angles			
S(1)—Ti—O(11)	79.94(9)	S(2)—Ti—O(21)	80.53(9)
S(3)—Ti—O(31)	80.37(9)	S(1)—Ti—O(31)	162.5(1)
S(2)—Ti—O(11)	160.1(2)	S(3)—Ti—O(21)	161.1(1)
S(1)—Ti—O(21)	107.72(9)	S(2)—Ti—O(31)	104.8(1)
S(3)—Ti—O(11)	103.9(1)	S(1)—Ti—S(2)	84.97(5)
S(1)—Ti—S(3)	85.70(5)	S(2)—Ti—S(3)	87.69(5)
O(11)—Ti—O(21)	91.8(1)	O(11)—Ti—O(31)	93.2(1)
O(21)—Ti—O(31)	88.4(1)	Ti—S(1)—C(16)	96.9(2)
Ti—S(2)—C(26)	97.8(2)	Ti—S(3)—C(36)	98.4(2)
Ti—O(11)—C(11)	124.6(3)	Ti—O(21)—C(21)	125.7(3)
Ti—O(31)—C(31)	127.3(3)	O(1)—Na—O(2)	97.4(1)
O(1)—Na—O(11′)	83.0(1)	O(1)—Na—O(21′)	85.5(1)
O(1)—Na—O(31)	110.3(1)	O(2)—Na—O(11′)	112.6(1)
O(2)—Na—O(21)	87.7(1)	O(2)—Na—O(31)	79.0(1)
O(21)—Na—O(31)	66.8(2)	O(21)—Na—O(11′)	98.6(1)
O(21)—Na—O(21)	89.2(1)	O(31)—Na—O(21′)	98.7(1)
O(11′)—Na—O(21)	69.0(1)	O(1)—Na—O(21)	173.6(1)
O(2)—Na—O(21′)	176.8(1)	O(31)—Na—O(11′)	161.7(1)
Ti—O(21)—Na	98.6(1)	Ti—O(31)—Na	106.2(1)
Ti—O(11)—Na′	99.7(1)	Ti—O(21)—Na′	99.5(1)
Na—O(21)—N′	90.77(6)		

[a] Symmetry code: *2–x, –y, 2–z*

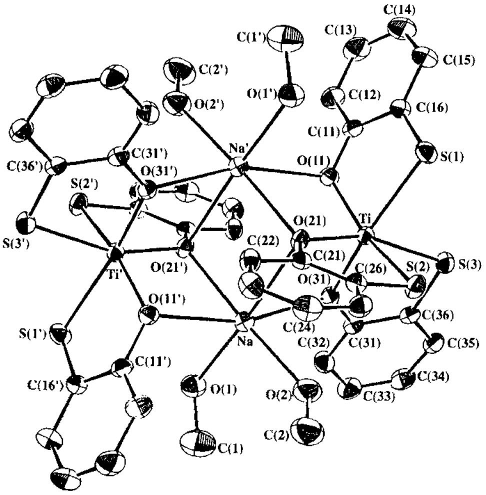


FIGURE 1 ORTEP structure of the anion $[Ti(mp)_3Na(MeOH)_2]_2^{2-}$ showing 40% probability ellipsoids. H atoms are omitted for clarity.

The title compound is isostructural but not isoelectronic with $(Et_4N)_2[V(mp)_3Na(MeOH)_2]_2$ (**2**).[9b] A comparison of pertinent atomic distances and bond angles is summarized in Table IV.

TABLE IV Average atomic distances (Å) and angles (°) in complexes $(Et_4N)_2[M(mp)_3Na(MeOH)_2]_2$ or (**1**) and M = V for (**2**)

Complex	(*1*)	(*2*)
M—S	2.428(1)	2.361(4)
M—O	1.949(3)	1.949(8)
M...M′	5.838	5.965
M...Na	3.425	3.432
Na...Na′	3.583	3.399
Na—O (MeOH)	2.385(4)	2.420(14)
Na—O (mp)	2.469(3)	2.429(10)
C—S	1.760(5)	1.750(10)
Bite O...S	2.846	2.834
Bite S—M—O	80.28(9)	81.6(3)
Trans S—M—O	161.2(1)	161.4(3)
M—S—C	97.7(2)	98.7(4)
M—O—C	125.9(3)	124.1(7)
Trans O—Na—O	170.7(1)	172.6(4)

As in $[V(mp)_3Na(MeOH)_2]_2^{2-}$, the dimeric assembly of (**1**) possesses a crystallographic centre of symmetry. The anion consists of two $[Ti(mp)_3]^{2-}$ units held together by two completely caged sodium ions with indirect Ti—Na bonds *via* bridging oxygen atoms from the mp ligands. This disposition yield a heterometallic tetranuclear $Ti_2Na_2O_6$ core, which can be interpreted as two corner-voided oxocubane-like $TiNa_2O_4$ subunits sharing a rhombic face NaO(21)Na′O(21′) (See Figure 2). All Ti···Ti, Ti···Na and Na···Na relationships are indirect metal-metal contacts. Ti···Ti and Na···Na distances are 5.838 and 3.583 Å, respectively, while Ti···Na and Ti···Na′ distances are 3.456 and 3.394 Å, respectively.

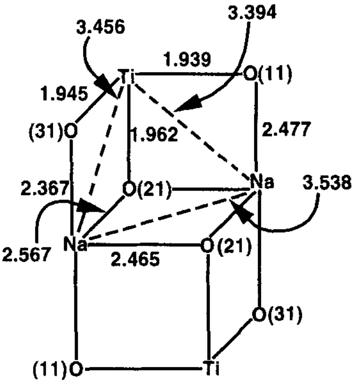


FIGURE 2 Illustration of twin corner-voided cubane-like $Ti_2Na_2O_6$ core.

The TiO(21)NaO(31) and TiO(21)Na′O(11) groups are perfectly coplanar with maximum deviations of 0.001 and 0.007 Å, respectively, from least-squares planes with a dihedral angle of 87.4°. The incomplete twin cubane-like skeleton is a new type of cluster topology in 2-mercaptophenol ligated complexes.

Each Ti atom is chelated by three bidentate mp ligands with $S_tO_{b\text{-}D}$ and $S_tO_{b\text{-}T}$ coordination modes, respectively, to form a $[Ti(mp)_3]^{2-}$ unit whose structure is similar to that of $[V(mp)_3]^{2-}$ in (**2**). The *facial* arrangement of the TiO_3S_3 core displays a distorted octahedral geometry in which each oxygen atom is opposite to a sulfur atom from the neighboring ligand. The mean value of *trans* S—Ti—O angles is 161.2°, and is attributed to the small bite angle of the bidentate ligands (av. 80.28°).[20a] Two types of Ti—O bonds are observed in the complex, Ti—μ_3—O in $S_tO_{b\text{-}T}$ mode and Ti—μ_2—O in $S_tO_{b\text{-}D}$ modes, where the former (1.962 Å) is longer than the latter (av. 1.942 Å). This μ_3—O exerts a weak *Trans* Influence on the sulfur atom opposite it; Ti—S(3) (2.417 Å) is shorter by 0.019 Å on average than the other two Ti—S bonds opposite to the μ_2—O atoms (Ti—S(1) 2.434 Å, Ti—S(2) 2.437 Å). The mean Ti—S distance (2.429 Å) agrees well with those reported for other *tris* chelated dithiolatotitanium(IV) complexes, *i.e.*, $[Ti(edt)_3]^{2-}$ (av. 2.428 Å),[6] $[Ti(DDDT)_3]^{2-}$ (av. 2.423 Å) [DDDT=5,6-dihydro-1,4-dithii-2,3-dithiolate][20a] and $[Ti(S_2C_6H_4)_3]^{2-}$ (av. 2.428 Å).[20b]

The $[Ti(mp)_3]^{2-}$ unit exhibits a *pseudo*-C_3 symmetry with the C_3 axis perpendicular to the parallel trigonal planes S(1)S(2)S(3) and O(11)O(21)O(31) (dihedral angle 2.5°). The five-membered chelate rings C(*n*1)-O(*n*1)-Ti-S(*n*)-C(*n*6) (*n* = 1, 2, 3) are nearly planar with maximum deviations of 0.152, 0.056 and 0.023 Å, respectively. C—S bonds (av. 1.760 Å) and C—O (av. 1.353 Å) and the Ti—O—C angles (av. 125.9°) and Ti—S—C (av. 97.7°) in the chelate rings fall in the range found for other mp chelate complexes.[3,8–10] The average bite angle of 80.3° together with the average bite distance of 2.846 Å is similar to lose with complex (**2**) (81.6° and 2.834 Å, respectively)[9b] and also within the range for a series of mp chelate complexes, exhibiting again the rigidity of the five-membered chelate ring.[3,9]

The coordination environment of the Na^+ ion is a distorted octahedron. Each Na^+ ion is surrounded by two μ_2-O and two μ_3-O atoms from the mp ligands of two $[Ti(mp)_3]^{2-}$ units, and octahedral coordination is completed by two terminal methanol molecules. The hydroxyl protons of the methanol molecules are hydrogen bonded to arylthiolato atoms[23] with S(1′)···H(1) and S(2)···H(2) distances of 2.320(1) and 2.427(1) Å, respectively, and corresponding angles S(1′)···H(1)—O(1) and S(2)···H(2)—O(2) are 167.2 and 157.0°, respectively (Figure 3).

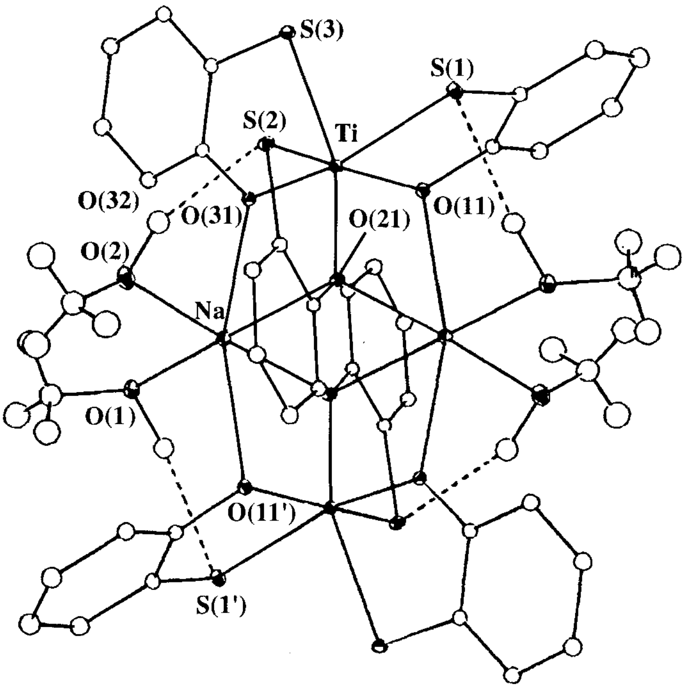


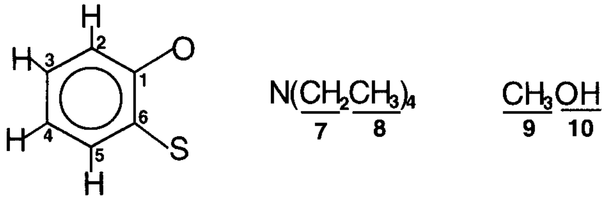
FIGURE 3 Perspective view of $[Ti(mp)_3Na(MeOH)_2]_2^{2-}$ showing hydrogen bonding interactions.

These H···S distances are significantly shorter than the sum of the (Van der Waals radii for H and S (3.05 Å).[23–24] Consequently, the O(1)···S(1′) and O(2···S(2) distances of 3.444(4) and 3.487(4) Å, respectively, are all in the range of normal O—H···S interactions.[25,26] The Na—O distances, in the range 2.367–2.567 Å of rather weak Na—O interactions are comparable to those reported in $[Na_3Co_4(\mu_3\text{-}O)_2(mpo)_8(DMF)_4]^+$ (2.25–2.63 Å),[13] $[Mo_2O_3(mp)_3Na(EtOH)_3]_2^{2-}$(2.26–2.60 Å),[27] $[\{V(mp)_3\}_2Na]^{3-}$ (2.361–2.500 Å)[9c] and complex (**2**) (2.366–2.510 Å).[9b]

IR spectra (KBr pellet) of (**1**) showed strong absorption bands at 613 cm^{-1} arising from the Ti-O stretch in agreement with those observed in $Ti(Me_2dtp)_2(OPr^i)_2$ ($Me_2dtp = S_2P(OMe)_2$, 615 cm^{-1}) and $Ti(S_2PMe_2)_2(OPr^i)_2$ (611 cm^{-1}).[28] The medium bands at 436 and 376 cm^{-1} are assignable to υ(Ti–S) stretching modes comparable to literature data for $[Ti(DDDT)_3]^{2-}$ (420, 345 cm^{-1})[20a] and $Ti(Me_2dtp)_2(OPr^i)_2$ (376, 354 cm^{-1}).[28]

The electronic spectrum of (**1**) in DMF showed two absorptions at 270 nm (ε = 41617 M^{-1} cm^{-1}) and 300 (54891), readily assignable to ligand $\pi \rightarrow \pi^*$ transitions. The remaining two bands at 410 (12573) and 464 (10723) are caused by ligand (π) → titanium (*d*) charge-transfer transitions, comparable to other six-coordinate dithiolatotitanium(IV) compounds.[18,20b]

^{1}H and ^{13}C NMR spectra exhibit expected diamagnetic characteristics with data given in Table V and proton and carbon assignments shown below.



The protons in the symmetry related mp ligands are well-defined by peaks at 6.142 ppm (d, H-2), 6.333 (t, H-4), 6.525 (t, H-3) and 6.700 (d, H-5) with intensity ratios 1:1:1:1, indicating only one type of the mp ligands in solution. The two sharp doublets correspond to the two α-H (H-2, H-5) atoms of mp, and the two triplets to the two *β*-H (H-4, H-3) atoms. Compared to the NMR data of the terminal phenyl groups in $[Pd_2(mp)_2(Hmp)_2]^{2-}$,[29] the upfield shifts are tentatively ascribed to H-2 and H-4 due to the p-π conjugation effect of the neighboring oxygen atom. ^{1}H-^{1}H COSY spectra show the correctness of these assignments (Figure 4a). The hydroxyl proton (H-10) of CH_3OH appears as a quadruplet at 4.122 ppm, for which no correlation is observed in the ^{1}H-^{13}C HMQC spectrum. The methyl signal (H-8) of tetraethylammonium ion at 1.124 ppm is readily assignable, but the resonance of methyl protons (H-9) of CH_3OH is immersed in that of the $-CH_2$ protons (H-7) of the Et_4N^+ ion, which can be distinguished by the ^{1}H-^{1}H COSY technique. The signal at *ca* 3.166 ppm correlating to 4.122 ppm (H-10) in the COSY spectrum (Figure 4b) is assigned to H-9. The shift at *ca* 3.158 ppm correlating to 1.124 ppm (H-8) is assigned to H-7. The ^{13}C NMR spectrum was assigned with the aid of ^{1}H-^{13}C HMQC technique; (See Table V). Integration of the ^{1}H NMR spectrum is consistent with the formulation of complex (**1**).

TABLE V NMR spectroscopic data for (**1**) in DMSO Solution

No.	*Chemical Shifts δ_H(ppm)*	*Coupling Constant J (Hz)*	*Integration*	*HMQC δ_C(ppm)*	*^{1}H-^{1}H COSY*
1				165.191	
2	6.142 (d)	$^3J_{2,3} = 7.5$	6	111.458	H-3
3	6.525 (t)	$^3J_{3,2} = 7.5$, $^3J_{3,4} = 7.5$	6	120.564	H-2, H-4
4	6.333 (t)	$^3J_{3,4} = 7.5$, $^3J_{4,5} = 7.0$	6	116.841	H-3, H-5
5	6.700 (d)	$^3J_{5,4} = 7.0$	6	126.654	H-4
6				144.757	
7	3.158 (q)	$^3J_{7,8} = 7.5$	16	51.474	H-8
8	1.124 (t-t)	$^3J_{8,7} = 7.5$	24	7.153	H-7
9	3.166 (d)	$^3J_{10,9} = 5$	12	48.662	H-10
10	4.122 (q)	$^3J_{10,9} = 5$	4		H-9

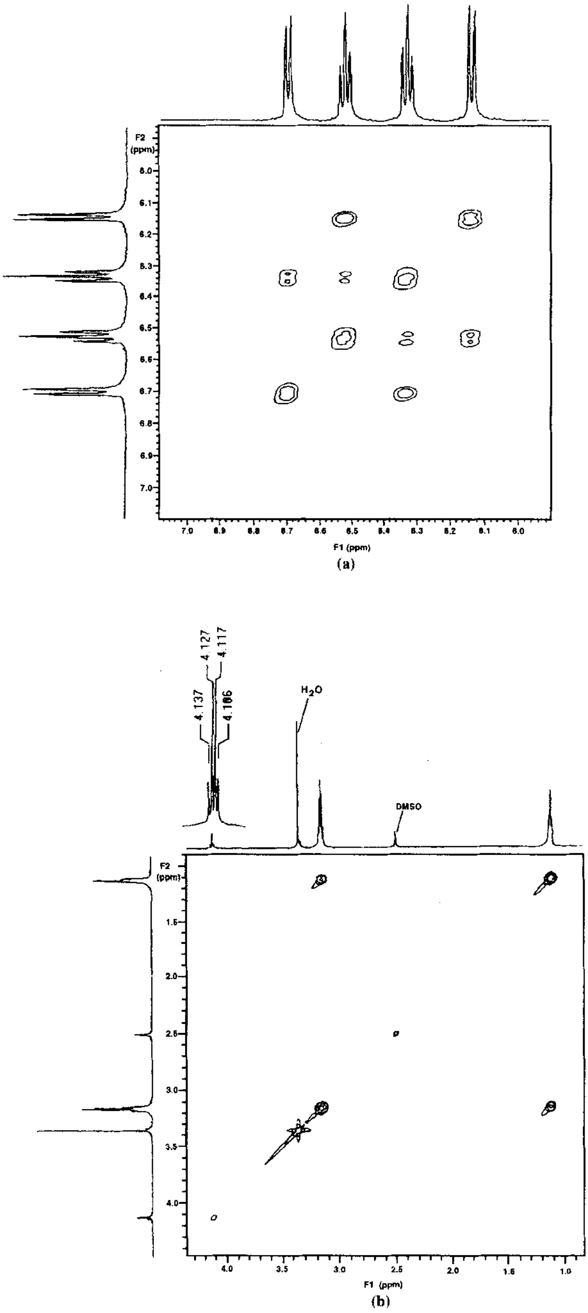


FIGURE 4 ^{1}H-^{1}H COSY spectrum of (**1**): a, low field region; b, high field region.

As shown by the NMR data, there is only one type of mp ligands in solution and no hydrogen-bonding is observed. Because of the rather weak Na-O interactions (av. 2.441 Å), it is believed that the dimeric anion in the solid state dissociates into two $[Ti(mp)_3]^{2-}$ units in solution at room temperature, just as was the case for the $[V(mp)_3Na(MeOH)_2]_2^{2-}$.[9b]

Supplementary Material

List of observed and calculated structure factors, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atoms parameters as well as a complete list of bond distances and angles are available from the authors on request.

Acknowledgments

We greatly appreciate the National Key Project for Fundamental Research, the NNSF of China and the NSF of Fujian Province for financial support of this work.

References

[1] Some key references are: (a) J.A. Kovacs and R.H. Holm, *Inorg. Chem.*, **26**, 711 (1987); (b) J.K. Rambo, J.C. Huffman and G. Christou, *J. Am. Chem. Soc.*, **111**, 8027 (1989); (c) B. Krebs and G. Henkel, *Angew. Chem. Int. Ed. Engl.*, **30**, 769 (1991).

[2] (a) D.W. Stephan, *Coord. Chem. Rev.*, **95**, 42 (1989); (b) T.T. Nadasdi, Y.J. Huang and D.W. Stephan, *Inorg. Chem.*, **32**, 347 (1993); (c) T.T. Nadasdi and D.W. Stephan, *Inorg. Chem.*, **32**, 3022 (1993).

[3] B.S. Kang, M.C. Hong, T.B. Wen, H.Q. Liu and J.X. Lu, *J. Cluster Science*, **6**, 379 (1995).

[4] (a) J.K. Money, J.C. Huffman and G. Christou, *Inorg. Chem.*, **27**, 507 (1988); (b) T.R. Halbert, and E.I. Stiefel, *Inorg. Chem.*, **28**, 2501 (1989); (c) D.D. Heinrich and J.P. Fackler, *Inorg. Chem.*, **29**, 4402 (1990).

[5] (a) H.J. Heeg, E.L. Blim and E. Deutsch, *Inorg. Chem.*, **24**, 1118 (1985); (b) G. Henkel, B. Krebs and W. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **31**, 1366 (1992).

[6] (a) J.R. Dorfman, C.P. Rao and R.H. Holm, *Inorg. Chem*, **24**, 453 (1985); (b) C.P. Rao, J.R. Dorfman and R.H. Holm, *Inorg. Chem.*, **25**, 428 (1986).

[7] J.R. Nicholson, G. Christou, D.J. Wang, J.C. Huffman, H.R. Chang and D.N. Hendrickson, *Polyhedron*, **10**, 2255 (1991).

[8] B.S. Kang, L.H. Weng, D.X. Wu, F. Wang, Z. Guo, L.R. Huang, Z.Y. Huang and H.Q. Liu, *Inorg. Chim. Acta*, **148**, 147 (1988).

[9] (a) B.S. Kang, L.H. Weng, H.Q. Liu, D.X. Wu, L.R. Huang, C.Z. Lu, J.H. Cai, X.T. Chen and J.X. Lu, *Inorg. Chem.*, **29**, 4873 (1990); (b) L.H. Weng, B.S. Kang, X.T. Chen, M.C. Hong, X.J. Lei, Y.H. Hu and H.Q. Liu, *Chin. J. Chem.*, **11**, 30 (1993); (c) T.B. Wen, Y.J. Xu, J.C. Shi, Y.H. Deng, C.N. Chen, Q.T. Liu and B.S. Kang, *Chin. J. Struct. Chem.*, **14**, 151 (1995).

[10] J.C. Shi, X.Y. Huang, T.B. Wen, Y.H. Deng, C.N. Chen, Q.T. Liu and B.S. Kang, *Chin. J. Struct. Chem.*, **14**, 293 (1995).

[11] X.T. Chen, L.H. Weng and B.S. Kang, *Chin. J. Struct. Chem.*, **10**, 227 (1991).

[12] X.T. Chen, Y.H. Hu, D.X. Wu, L.H. Weng and B.S. Kang, *Polyhedron*, **10**, 2651 (1991).

[13] F.L. Jiang, M.C. Hong, X.L. Xie, R. Cao, B.S. Kang, D.X. Wu and H.Q. Liu, *Inorg. Chim. Acta*, **231**, 153 (1995).

[14] P. Kopf-Maier and H. Kopf, *Chem. Rev.*, **87**, 1137 (1987).

[15] L.K. Myers, I. Langholf and M.E. Thompson, *J. Am. Chem. Soc.*, **114**, 7560 (1992).

[16] C.G. Carraher, *J. Polym. News.*, **15**, 301 (1990).

[17] (a) $Cp_2Ti(SPh)_2$: G. Müller, S.F. Watkins and L.F. Dahl, *J Organomet. Chem.*, **111**, 73 (1976); (b) $Cp_2Ti(SMe)_2$: A.A.F. Mara, C.T. Carrondo and G.A. Jeffery, *Acta Cryst.*, **C39**, 42 (1983).

[18] J.L. Martin and J. Takats, *Inorg. Chem.*, **14**, 73 (1975).

[19] (a) G.W. Svetich and A.A. Voge, *Acta Cryst.*, **B28**, 1760 (1972); (b) J.A. Ibers, *Nature*, **197**, 686 (1963); (c) D.A. Wright and D.A. Willams, *Acta Cryst.*, **B24**, 1107 (1968).

[20] (a) $[Ti(DDDT)_3]^{2-}$: J.H. Welch, R.D. Bereman and P. Singh, *Inorg. Chem.*, **29**, 68 (1990); (b) $[Ti(bdt)_3]^{2-}$: M. Könemann, W. Stiier, K. Kirschbaum and D.M. Giolando, *Polyhedron*, **9**, 1415 (1994).

[21] G. Wilkinson and J.M. Birmingham, *J. Am. Chem. Soc.*, **76**, 4281 (1954).

[22] *MolEN, An Interactive Structure Solution Procedure, (Enraf-Nonius, Delft, The Netherlands*), (1990).

[23] J.K. Money, J.C. Huffman and G. Christou, *Inorg. Chem.*, **24**, 3297 (1985).

[24] L. Pauling, *The Nature of the Chemical Bond*, (Cornell University Press, Ithaca, 1960), p 260.

[25] A. Preisinger, K. Mereiter, O. Baumgartner, G. Heger, W. Mikenda and H. Steidl, *Inorg. Chim. Acta*, **57**, 237 (1982).

[26] K. Mereiter, A. Preisinger and A. Zellner, *Inorg. Chim. Acta*, **72**, 67 (1983).

[27] B.S. Kang, Y.H. Hu, L.H. Weng, D.X. Wu, X.T. Chen, Y.J. Xu and J.X. Lu, *J. Inorg. Biochem.*, **46**, 231 (1992).

[28] H.M. Gau and R.C. Fay, *Inorg. Chem.* **29**, 4974 (1990).

[29] J.C. Shi, D.X. Wu, B.S. Kang, *et al.*, unpublished results.