ORGANOMETALLICS
Organometallics, 1996, 15(17), 3631-3633, DOI:10.1021/om960358x

For Supplementary Material

Experimental

Materials and Instrumentation. Reactions were carried out under inert atmosphere using standard Schlenk and glove box techniques. Reagent grade solvents were dried by distillation from the appropriate drying agents. NaH (Strem, 60% in oil) and NaD (Strem, 20% in oil) were washed with hexanes and the resulting solids were dried in vacuo. $Cp_2Ti(SH)_2$ was synthesized from Cp_2TiCl_2 and H_2S in the presence of Et_3N, according to the published procedure.[1]

Infrared and ^1H NMR spectra were recorded on a Bio Rad FTS-40 and a Bruker WM 300 , respectively.

Preparation of $\{Na_2[CpTi(m\text{-}S)(S)]_2 \cdot 4THF\}_2$ (1). In a glove box, $Cp_2Ti(SH)_2$ (0.052 g, 21 mmol) and NaH (0.005 g, 21 mmol) were mixed as solids. THF (3 mL) was added to the solids. The resultant red-orange solution was stirred and periodically evacuated for 5 min. since a small amount of gas, presumably H_2, was slowly evolved. Over this time, the solution turned from red-orange to green. The solution was then reduced in vacuo to a volume of approximately 1 mL. A THF/hexane diffusion was set up by placing the product solution in a small vial inside of a larger vial of hexanes. The THF in the inner vial slowly diffused to the hexanes, leaving dark green crystals of **1** in a green-brown supernatant solution. Complex **1** is very air and moisture sensitive. If THF is completely removed from solutions of **1** or if solvents such as hexanes, Et_2O or toluene are added to THF solutions of **1**, the product solution will change from dark green to yellow-brown. For this reason elemental analysis of **1** was not possible.

Yield: 0.045 g (62%) IR (KBr): 1438, 1015, 801(s), 466, 394, 386 cm^{-1}. ^1H NMR (THF-d_8): δ 6.10 (C_5H_5), 3.56, 1.76, 1.75, 1.74, 1.71 (C_4H_8O) ppm.[2]

X-Ray Crystallographic Analysis of $\{Na_2[CpTi(\mu\text{-}S)(S)]_2 \cdot 4THF\}_2$. A dark green parallelepiped shaped crystal was attached to a thin glass fiber using silicone grease.

The crystal was then immediately placed under a liquid. N_2 stream on a Siemens P4/PC diffractometer. The radiation used was graphite monachromatized Mo Kα radiation (λ= 0.71069 Å). The lattice parameters were optimized from a least-squares calculation on 32 carefully centered reflections of high Bragg angle. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction, including Lorentz and polarization corrections, structure solution and refinement, and graphics were performed using SHELXTL PC Version 4.2/360 software.[3] No absorption corrections were applied due to the low absorption coefficient of this material. Data collection parameters are given in Table I-III.

The structure was solved in space group $P\bar{1}$ using Patterson techniques to reveal the Ti and S atom positions. The remaining atoms appeared in subsequent Fourier synthesis. All hydrogen atoms were fixed in positions corresponding to a C-H distance of 0.96 Å using the HFIX facility in SHELXTL PC. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms. Hydrogen atoms had their isotropic temperature factors fixed at 0.08Å.[3] The final refinement converged to R= 0.0315 and R_w= 0.0402.

References

(1) a) Shaver, A.; McCall, J. M. *Organometallics* **1994**, *3*, 1823. b) Shaver, A.; Marmolejo, G.; McCall, J. M. *Inorg. Synth.* **1990**, *29*, 65.

(2) The coordinated THF resonances are broad and overlap with the THF-d_8 resonances (d 3.58, 1.73 ppm).

(3) XSCANS and SHELXTL PC are products of Siemens Analytical X-ray Instruments, Inc., 6300 Enterprise Lane, Madison, Wisconsin 53719.

TABLE 1. STRUCTURE DETERMINATION SUMMARY

Crystal Data

Empirical Formula	$C_{52}H_{84}Na_4O_8S_8Ti_4$
Color; Habit	Green Parallelepiped
Crystal size (mm)	0.21 x 0.28 x 0.37
Crystal System	Triclinic
Space Group	$P\bar{1}$
Unit Cell Dimensions	$a = 10.6300(10)$ Å
	$b = 11.3700(10)$ Å
	$c = 14.3960(10)$ Å
	$\alpha = 83.960(6)^\circ$
	$\beta = 80.410(6)^\circ$
	$\gamma = 70.370(6)^\circ$
Volume	$1613.7(3)$ Å^3
Z	1
Formula weight	1377.2
Density(calc.)	1.417 Mg/m^3
Absorption Coefficient	0.810 mm^{-1}
F(000)	720

Data Collection

Diffractometer Used	Siemens R3m/V
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	173
Monochromator	Highly oriented graphite crystal
2θ Range	7.0 to 45.0°
Scan Type	ω
Scan Speed	Variable; 4.00 to 30.00°/min. in ω
Scan Range (ω)	0.68°
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 0.5% of total scan time
Standard Reflections	3 measured every 97 reflections
Index Ranges	$-1 \leq h \leq 11$, $-11 \leq k \leq 12$ $-15 \leq l \leq 15$
Reflections Collected	5049
Independent Reflections	4227 (R_{int} = 5.93%)
Observed Reflections	3599 ($F > 4.0\sigma(F)$)
Absorption Correction	N/A

Solution and Refinement

System Used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	N/A
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
Number of Parameters Refined	343
Final R Indices (obs. data)	R = 3.15 %, wR = 4.02 %
R Indices (all data)	R = 4.13 %, wR = 4.19 %
Goodness-of-Fit	1.42
Largest and Mean Δ/σ	0.001, 0.000
Data-to-Parameter Ratio	10.5:1
Largest Difference Peak	0.41 $e\text{Å}^{-3}$
Largest Difference Hole	-0.40 $e\text{Å}^{-3}$

Table II. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U(eq)
Ti(1)	3262(1)	6855(1)	7249(1)	20(1)
Ti(2)	6135(1)	6114(1)	7924(1)	20(1)
S(1)	4120(1)	5748(1)	8590(1)	22(1)
S(2)	3575(1)	5479(1)	6194(1)	27(1)
S(3)	5034(1)	7684(1)	6849(1)	25(1)
S(4)	7332(1)	4482(1)	7117(1)	28(1)
Na(1)	5005(1)	3514(1)	7530(1)	26(1)
Na(2)	3808(1)	4297(1)	4505(1)	34(1)
O(1)	6261(2)	2020(2)	8628(2)	34(1)
O(2)	5820(2)	1963(2)	6416(2)	45(1)
O(3)	2071(2)	3507(3)	5116(2)	46(1)
O(4)	3097(2)	2882(2)	8159(2)	40(1)
C(1)	6667(3)	694(3)	8597(3)	39(1)
C(2)	8194(4)	244(4)	8512(3)	54(2)
C(3)	8505(4)	1285(4)	8897(3)	59(2)
C(4)	7158(4)	2245(3)	9168(3)	48(2)
C(5)	5263(4)	1190(3)	5997(3)	48(2)
C(6)	6413(4)	264(3)	5423(2)	37(1)
C(7)	7661(4)	346(3)	5765(2)	37(1)
C(8)	7204(4)	1698(3)	6020(3)	43(2)
C(9)	1527(3)	3352(3)	6081(2)	37(1)
C(10)	188(3)	2836(3)	5163(2)	39(1)
C(11)	777(4)	2442(3)	6074(2)	41(1)
C(12)	1262(3)	3230(3)	4517(2)	33(1)
C(13)	1845(3)	3805(3)	8487(2)	41(2)
C(14)	956(5)	3112(4)	8992(4)	85(3)
C(15)	1757(5)	1853(5)	9056(5)	135(4)
C(16)	3081(4)	1694(4)	8570(3)	55(2)
C(21)	6151(3)	7706(3)	8899(2)	32(1)
C(22)	7321(3)	7449(3)	8225(2)	33(1)
C(23)	8125(3)	6217(3)	8406(2)	35(1)
C(24)	7445(3)	5703(3)	9169(2)	32(1)
C(25)	6239(3)	6623(3)	9484(2)	30(1)
C(31)	882(3)	7494(3)	7273(3)	42(2)
C(32)	1326(3)	8392(3)	6747(2)	38(1)
C(33)	1807(3)	8984(3)	7337(3)	40(1)
C(34)	1667(4)	8438(3)	8234(3)	46(2)
C(35)	1098(3)	7492(3)	8192(3)	47(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3. Bond lengths (Å)

Ti(1)-Ti(2)	3.174	(1)	Ti(1)-S(1)	2.335	(1)
Ti(1)-S(2)	2.202	(1)	Ti(1)-S(3)	2.343	(1)
Ti(1)-Na(1)	3.637	(1)	Ti(1)-C(31)	2.381	(3)
Ti(1)-C(32)	2.371	(3)	Ti(1)-C(33)	2.398	(3)
Ti(1)-C(34)	2.410	(3)	Ti(1)-C(35)	2.389	(3)
Ti(1)-Na(2A)	3.623	(1)	Ti(2)-S(1)	2.348	(1)
Ti(2)-S(3)	2.360	(1)	Ti(2)-S(4)	2.187	(1)
Ti(2)-Na(1)	3.671	(2)	Ti(2)-C(21)	2.410	(4)
Ti(2)-C(22)	2.385	(4)	Ti(2)-C(23)	2.375	(4)
Ti(2)-C(24)	2.364	(4)	Ti(2)-C(25)	2.406	(3)
Ti(2)-Na(2A)	3.564	(1)	S(1)-Na(1)	2.898	(1)
S(2)-Na(1)	2.965	(1)	S(2)-Na(2)	2.836	(2)
S(2)-Na(2A)	2.882	(2)	S(3)-Na(2A)	2.941	(1)
S(4)-Na(1)	2.981	(2)	S(4)-Na(2A)	2.825	(1)
Na(1)-O(1)	2.405	(2)	Na(1)-O(2)	2.352	(3)
Na(1)-O(4)	2.384	(3)	Na(1)-Na(2A)	3.964	(2)
Na(2)-O(3)	2.322	(3)	Na(2)-Ti(1A)	3.623	(1)
Na(2)-Ti(2A)	3.564	(1)	Na(2)-S(2A)	2.882	(2)
Na(2)-S(3A)	2.941	(1)	Na(2)-S(4A)	2.825	(1)
Na(2)-Na(1A)	3.964	(2)	Na(2)-Na(2A)	3.927	(3)
O(1)-C(1)	1.426	(4)	O(1)-C(4)	1.424	(5)
O(2)-C(5)	1.438	(6)	O(2)-C(8)	1.429	(4)
O(3)-C(9)	1.431	(4)	O(3)-C(12)	1.438	(5)
O(4)-C(13)	1.432	(4)	O(4)-C(16)	1.421	(5)
C(1)-C(2)	1.517	(5)	C(2)-C(3)	1.510	(7)
C(3)-C(4)	1.499	(5)	C(5)-C(6)	1.506	(5)
C(6)-C(7)	1.524	(6)	C(7)-C(8)	1.514	(5)
C(9)-C(11)	1.504	(6)	C(10)-C(11)	1.508	(5)
C(10)-C(12)	1.508	(5)	C(13)-C(14)	1.482	(7)
C(14)-C(15)	1.401	(7)	C(15)-C(16)	1.425	(7)
C(21)-C(22)	1.409	(4)	C(21)-C(25)	1.402	(4)
C(22)-C(23)	1.398	(4)	C(23)-C(24)	1.398	(5)
C(24)-C(25)	1.395	(4)	C(31)-C(32)	1.371	(5)
C(31)-C(35)	1.380	(6)	C(32)-C(33)	1.390	(6)
C(33)-C(34)	1.381	(5)	C(34)-C(35)	1.410	(6)

Table 3. Bond angles (°)

Ti(2)-Ti(1)-S(1)	47.5(1)	Ti(2)-Ti(1)-S(2)	103.1(1)
S(1)-Ti(1)-S(2)	107.2(1)	Ti(2)-Ti(1)-S(3)	47.8(1)
S(1)-Ti(1)-S(3)	93.1(1)	S(2)-Ti(1)-S(3)	106.0(1)
Ti(2)-Ti(1)-Na(1)	64.8(1)	S(1)-Ti(1)-Na(1)	52.8(1)
S(2)-Ti(1)-Na(1)	54.6(1)	S(3)-Ti(1)-Na(1)	103.0(1)
Ti(2)-Ti(1)-C(31)	161.5(1)	S(1)-Ti(1)-C(31)	117.1(1)
S(2)-Ti(1)-C(31)	91.1(1)	S(3)-Ti(1)-C(31)	139.3(1)
Na(1)-Ti(1)-C(31)	116.7(1)	Ti(2)-Ti(1)-C(32)	150.4(1)
S(1)-Ti(1)-C(32)	142.4(1)	S(2)-Ti(1)-C(32)	98.0(1)
S(3)-Ti(1)-C(32)	106.4(1)	Na(1)-Ti(1)-C(32)	144.6(1)
C(31)-Ti(1)-C(32)	33.5(1)	Ti(2)-Ti(1)-C(33)	118.8(1)
S(1)-Ti(1)-C(33)	120.3(1)	S(2)-Ti(1)-C(33)	130.4(1)
S(3)-Ti(1)-C(33)	86.0(1)	Na(1)-Ti(1)-C(33)	168.4(1)
C(31)-Ti(1)-C(33)	56.0(1)	C(32)-Ti(1)-C(33)	33.9(1)
Ti(2)-Ti(1)-C(34)	108.9(1)	S(1)-Ti(1)-C(34)	89.5(1)
S(2)-Ti(1)-C(34)	147.1(1)	S(3)-Ti(1)-C(34)	101.0(1)
Na(1)-Ti(1)-C(34)	135.8(1)	C(31)-Ti(1)-C(34)	56.0(1)
C(32)-Ti(1)-C(34)	55.8(1)	C(33)-Ti(1)-C(34)	33.4(1)
Ti(2)-Ti(1)-C(35)	127.8(1)	S(1)-Ti(1)-C(35)	87.5(1)
S(2)-Ti(1)-C(35)	116.6(1)	S(3)-Ti(1)-C(35)	135.1(1)
Na(1)-Ti(1)-C(35)	112.5(1)	C(31)-Ti(1)-C(35)	33.6(1)
C(32)-Ti(1)-C(35)	55.9(1)	C(33)-Ti(1)-C(35)	56.1(1)
C(34)-Ti(1)-C(35)	34.2(1)	Ti(2)-Ti(1)-Na(2A)	62.8(1)
S(1)-Ti(1)-Na(2A)	99.6(1)	S(2)-Ti(1)-Na(2A)	52.7(1)
S(3)-Ti(1)-Na(2A)	54.0(1)	Na(1)-Ti(1)-Na(2A)	66.2(1)
C(31)-Ti(1)-Na(2A)	135.6(1)	C(32)-Ti(1)-Na(2A)	117.9(1)
C(33)-Ti(1)-Na(2A)	125.4(1)	C(34)-Ti(1)-Na(2A)	153.5(1)
C(35)-Ti(1)-Na(2A)	168.5(1)	Ti(1)-Ti(2)-S(1)	47.2(1)
Ti(1)-Ti(2)-S(3)	47.3(1)	S(1)-Ti(2)-S(3)	92.4(1)
Ti(1)-Ti(2)-S(4)	103.2(1)	S(1)-Ti(2)-S(4)	106.1(1)
S(3)-Ti(2)-S(4)	107.2(1)	Ti(1)-Ti(2)-Na(1)	63.7(1)
S(1)-Ti(2)-Na(1)	52.1(1)	S(3)-Ti(2)-Na(1)	101.7(1)
S(4)-Ti(2)-Na(1)	54.3(1)	Ti(1)-Ti(2)-C(21)	109.2(1)
S(1)-Ti(2)-C(21)	101.5(1)	S(3)-Ti(2)-C(21)	89.7(1)
S(4)-Ti(2)-C(21)	146.7(1)	Na(1)-Ti(2)-C(21)	151.1(1)
Ti(1)-Ti(2)-C(22)	128.7(1)	S(1)-Ti(2)-C(22)	135.6(1)
S(3)-Ti(2)-C(22)	88.5(1)	S(4)-Ti(2)-C(22)	115.9(1)
Na(1)-Ti(2)-C(22)	167.5(1)	C(21)-Ti(2)-C(22)	34.2(1)
Ti(1)-Ti(2)-C(23)	162.9(1)	S(1)-Ti(2)-C(23)	139.2(1)
S(3)-Ti(2)-C(23)	118.6(1)	S(4)-Ti(2)-C(23)	90.1(1)
Na(1)-Ti(2)-C(23)	133.4(1)	C(21)-Ti(2)-C(23)	56.6(1)
C(22)-Ti(2)-C(23)	34.2(1)	Ti(1)-Ti(2)-C(24)	149.2(1)
S(1)-Ti(2)-C(24)	105.3(1)	S(3)-Ti(2)-C(24)	144.0(1)
S(4)-Ti(2)-C(24)	97.7(1)	Na(1)-Ti(2)-C(24)	114.0(1)
C(21)-Ti(2)-C(24)	56.5(1)	C(22)-Ti(2)-C(24)	56.9(1)
C(23)-Ti(2)-C(24)	34.3(1)	Ti(1)-Ti(2)-C(25)	118.3(1)
S(1)-Ti(2)-C(25)	85.7(1)	S(3)-Ti(2)-C(25)	120.4(1)
S(4)-Ti(2)-C(25)	130.5(1)	Na(1)-Ti(2)-C(25)	121.8(1)
C(21)-Ti(2)-C(25)	33.8(1)	C(22)-Ti(2)-C(25)	56.6(1)
C(23)-Ti(2)-C(25)	56.6(1)	C(24)-Ti(2)-C(25)	34.0(1)
Ti(1)-Ti(2)-Na(2A)	64.8(1)	S(1)-Ti(2)-Na(2A)	101.0(1)
S(3)-Ti(2)-Na(2A)	55.1(1)	S(4)-Ti(2)-Na(2A)	52.4(1)
Na(1)-Ti(2)-Na(2A)	66.4(1)	C(21)-Ti(2)-Na(2A)	138.7(1)
C(22)-Ti(2)-Na(2A)	115.2(1)	C(23)-Ti(2)-Na(2A)	118.1(1)
C(24)-Ti(2)-Na(2A)	145.0(1)	C(25)-Ti(2)-Na(2A)	171.8(1)
Ti(1)-S(1)-Ti(2)	85.3(1)	Ti(1)-S(1)-Na(1)	87.4(1)

Ti(2)-S(1)-Na(1)	88.1(1)	Ti(1)-S(2)-Na(1)	88.2(1)
Ti(1)-S(2)-Na(2)	164.5(1)	Na(1)-S(2)-Na(2)	106.6(1)
Ti(1)-S(2)-Na(2A)	89.9(1)	Na(1)-S(2)-Na(2A)	85.4(1)
Na(2)-S(2)-Na(2A)	86.7(1)	Ti(1)-S(3)-Ti(2)	84.9(1)
Ti(1)-S(3)-Na(2A)	85.8(1)	Ti(2)-S(3)-Na(2A)	83.7(1)
Ti(2)-S(4)-Na(1)	89.1(1)	Ti(2)-S(4)-Na(2A)	89.7(1)
Na(1)-S(4)-Na(2A)	86.1(1)	Ti(1)-Na(1)-Ti(2)	51.5(1)
Ti(1)-Na(1)-S(1)	39.9(1)	Ti(2)-Na(1)-S(1)	39.7(1)
Ti(1)-Na(1)-S(2)	37.2(1)	Ti(2)-Na(1)-S(2)	78.9(1)
S(1)-Na(1)-S(2)	77.1(1)	Ti(1)-Na(1)-S(4)	79.1(1)
Ti(2)-Na(1)-S(4)	36.6(1)	S(1)-Na(1)-S(4)	76.2(1)
S(2)-Na(1)-S(4)	89.1(1)	Ti(1)-Na(1)-O(1)	139.8(1)
Ti(2)-Na(1)-O(1)	96.8(1)	S(1)-Na(1)-O(1)	100.2(1)
S(2)-Na(1)-O(1)	175.7(1)	S(4)-Na(1)-O(1)	86.9(1)
Ti(1)-Na(1)-O(2)	130.7(1)	Ti(2)-Na(1)-O(2)	132.0(1)
S(1)-Na(1)-O(2)	168.6(1)	S(2)-Na(1)-O(2)	94.2(1)
S(4)-Na(1)-O(2)	96.7(1)	O(1)-Na(1)-O(2)	88.0(1)
Ti(1)-Na(1)-O(4)	98.1(1)	Ti(2)-Na(1)-O(4)	134.4(1)
S(1)-Na(1)-O(4)	94.7(1)	S(2)-Na(1)-O(4)	95.2(1)
S(4)-Na(1)-O(4)	168.8(1)	O(1)-Na(1)-O(4)	88.3(1)
O(2)-Na(1)-O(4)	93.3(1)	Ti(1)-Na(1)-Na(2A)	56.7(1)
Ti(2)-Na(1)-Na(2A)	55.5(1)	S(1)-Na(1)-Na(2A)	83.3(1)
S(2)-Na(1)-Na(2A)	46.4(1)	S(4)-Na(1)-Na(2A)	45.3(1)
O(1)-Na(1)-Na(2A)	130.2(1)	O(2)-Na(1)-Na(2A)	85.5(1)
O(4)-Na(1)-Na(2A)	141.2(1)	S(2)-Na(2)-O(3)	92.3(1)
S(2)-Na(2)-Ti(1A)	129.1(1)	O(3)-Na(2)-Ti(1A)	131.5(1)
S(2)-Na(2)-Ti(2A)	160.4(1)	O(3)-Na(2)-Ti(2A)	97.8(1)
Ti(1A)-Na(2)-Ti(2A)	52.4(1)	S(2)-Na(2)-S(2A)	93.3(1)
O(3)-Na(2)-S(2A)	163.3(1)	Ti(1A)-Na(2)-S(2A)	37.4(1)
Ti(2A)-Na(2)-S(2A)	81.8(1)	S(2)-Na(2)-S(3A)	155.7(1)
O(3)-Na(2)-S(3A)	91.5(1)	Ti(1A)-Na(2)-S(3A)	40.1(1)
Ti(2A)-Na(2)-S(3A)	41.2(1)	S(2A)-Na(2)-S(3A)	77.1(1)
S(2)-Na(2)-S(4A)	124.5(1)	O(3)-Na(2)-S(4A)	95.8(1)
Ti(1A)-Na(2)-S(4A)	81.4(1)	Ti(2A)-Na(2)-S(4A)	37.9(1)
S(2A)-Na(2)-S(4A)	94.0(1)	S(3A)-Na(2)-S(4A)	78.8(1)
S(2)-Na(2)-Na(1A)	104.8(1)	O(3)-Na(2)-Na(1A)	144.3(1)
Ti(1A)-Na(2)-Na(1A)	57.1(1)	Ti(2A)-Na(2)-Na(1A)	58.1(1)
S(2A)-Na(2)-Na(1A)	48.2(1)	S(3A)-Na(2)-Na(1A)	85.6(1)
S(4A)-Na(2)-Na(1A)	48.6(1)	S(2)-Na(2)-Na(2A)	47.1(1)
O(3)-Na(2)-Na(2A)	137.0(1)	Ti(1A)-Na(2)-Na(2A)	82.7(1)
Ti(2A)-Na(2)-Na(2A)	125.2(1)	S(2A)-Na(2)-Na(2A)	46.1(1)
S(3A)-Na(2)-Na(2A)	119.7(1)	S(4A)-Na(2)-Na(2A)	117.4(1)
Na(1A)-Na(2)-Na(2A)	72.3(1)	Na(1)-O(1)-C(1)	125.8(2)
Na(1)-O(1)-C(4)	125.0(2)	C(1)-O(1)-C(4)	105.1(2)
Na(1)-O(2)-C(5)	135.9(2)	Na(1)-O(2)-C(8)	115.4(2)
C(5)-O(2)-C(8)	108.6(3)	Na(2)-O(3)-C(9)	128.6(2)
Na(2)-O(3)-C(12)	121.8(2)	C(9)-O(3)-C(12)	109.2(3)
Na(1)-O(4)-C(13)	119.5(2)	Na(1)-O(4)-C(16)	128.1(2)
C(13)-O(4)-C(16)	108.7(3)	O(1)-C(1)-C(2)	105.6(3)
C(1)-C(2)-C(3)	103.9(3)	C(2)-C(3)-C(4)	105.0(4)
O(1)-C(4)-C(3)	105.8(3)	O(2)-C(5)-C(6)	107.5(3)
C(5)-C(6)-C(7)	103.6(3)	C(6)-C(7)-C(8)	101.9(3)
O(2)-C(8)-C(7)	104.6(3)	O(3)-C(9)-C(11)	104.7(3)
C(11)-C(10)-C(12)	103.3(3)	C(9)-C(11)-C(10)	101.8(3)
O(3)-C(12)-C(10)	106.4(3)	O(4)-C(13)-C(14)	106.4(3)
C(13)-C(14)-C(15)	106.5(4)	C(14)-C(15)-C(16)	110.3(5)
O(4)-C(16)-C(15)	107.3(3)	Ti(2)-C(21)-C(22)	71.9(2)
Ti(2)-C(21)-C(25)	72.9(2)	C(22)-C(21)-C(25)	107.9(3)
Ti(2)-C(22)-C(21)	73.9(2)	Ti(2)-C(22)-C(23)	72.6(2)

C(21)-C(22)-C(23)	107.7(3)	Ti(2)-C(23)-C(22)	73.3(2)
Ti(2)-C(23)-C(24)	72.4(2)	C(22)-C(23)-C(24)	108.1(3)
Ti(2)-C(24)-C(23)	73.3(2)	Ti(2)-C(24)-C(25)	74.7(2)
C(23)-C(24)-C(25)	108.4(3)	Ti(2)-C(25)-C(21)	73.2(2)
Ti(2)-C(25)-C(24)	71.3(2)	C(21)-C(25)-C(24)	107.9(3)
Ti(1)-C(31)-C(32)	72.8(2)	Ti(1)-C(31)-C(35)	73.5(2)
C(32)-C(31)-C(35)	108.5(4)	Ti(1)-C(32)-C(31)	73.6(2)
Ti(1)-C(32)-C(33)	74.1(2)	C(31)-C(32)-C(33)	108.6(3)
Ti(1)-C(33)-C(32)	72.0(2)	Ti(1)-C(33)-C(34)	73.8(2)
C(32)-C(33)-C(34)	107.8(4)	Ti(1)-C(34)-C(33)	72.8(2)
Ti(1)-C(34)-C(35)	72.1(2)	C(33)-C(34)-C(35)	107.6(4)
Ti(1)-C(35)-C(31)	72.9(2)	Ti(1)-C(35)-C(34)	73.7(2)
C(31)-C(35)-C(34)	107.5(3)		

Table 4. Anisotropic displacement coefficients ($Å^2 x 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1)	21(1)	21(1)	19(1)	-7(1)	-2(1)	-2(1)
Ti(2)	22(1)	19(1)	20(1)	-10(1)	-2(1)	-2(1)
S(1)	24(1)	23(1)	20(1)	-10(1)	-3(1)	0(1)
S(2)	30(1)	32(1)	23(1)	-13(1)	-3(1)	-7(1)
S(3)	30(1)	23(1)	24(1)	-13(1)	-4(1)	3(1)
S(4)	28(1)	26(1)	31(1)	-9(1)	2(1)	-9(1)
Na(1)	27(1)	22(1)	30(1)	-9(1)	-1(1)	-5(1)
Na(2)	36(1)	48(1)	26(1)	-23(1)	2(1)	-11(1)
O(1)	37(1)	25(1)	40(1)	-4(1)	-13(1)	-5(1)
O(2)	43(2)	38(1)	56(2)	-16(1)	9(1)	-24(1)
O(3)	47(2)	79(2)	27(1)	-42(1)	-3(1)	-5(1)
O(4)	30(1)	41(1)	48(1)	-15(1)	-1(1)	2(1)
C(1)	39(2)	24(2)	53(2)	-7(2)	-14(2)	-1(2)
C(2)	39(2)	56(3)	59(3)	2(2)	-14(2)	-19(2)
C(3)	41(3)	91(3)	57(3)	-35(2)	-5(2)	-14(2)
C(4)	75(3)	33(2)	43(2)	-14(2)	-30(2)	-3(2)
C(5)	48(2)	51(2)	49(2)	-16(2)	-5(2)	-18(2)
C(6)	50(2)	30(2)	33(2)	-13(2)	-7(2)	-7(2)
C(7)	43(2)	29(2)	38(2)	-9(2)	-4(2)	-7(2)
C(8)	41(2)	39(2)	52(2)	-20(2)	7(2)	-15(2)
C(9)	34(2)	52(2)	23(2)	-12(2)	-3(2)	-1(2)
C(10)	31(2)	47(2)	44(2)	-16(2)	-2(2)	-13(2)
C(11)	40(2)	43(2)	38(2)	-17(2)	7(2)	-1(2)
C(12)	36(2)	39(2)	31(2)	-16(2)	-12(2)	-2(2)
C(13)	36(2)	52(2)	39(2)	-15(2)	-7(2)	-8(2)
C(14)	53(3)	86(4)	123(5)	-45(3)	38(3)	-45(3)
C(15)	39(3)	109(5)	235(8)	-33(3)	-14(4)	102(5)
C(16)	53(3)	46(2)	67(3)	-22(2)	-2(2)	1(2)
C(21)	38(2)	28(2)	35(2)	-12(2)	-12(2)	-10(2)
C(22)	43(2)	37(2)	31(2)	-27(2)	-11(2)	-2(2)
C(23)	26(2)	48(2)	37(2)	-18(2)	-8(2)	-10(2)
C(24)	38(2)	32(2)	35(2)	-15(2)	-20(2)	1(2)
C(25)	40(2)	42(2)	18(2)	-23(2)	-8(2)	-5(1)
C(31)	20(2)	48(2)	57(3)	-6(2)	-5(2)	-12(2)
C(32)	29(2)	42(2)	34(2)	0(2)	-9(2)	5(2)
C(33)	31(2)	23(2)	60(3)	0(2)	-7(2)	-1(2)
C(34)	36(2)	47(2)	40(2)	15(2)	-12(2)	-23(2)
C(35)	26(2)	48(2)	44(2)	4(2)	13(2)	11(2)

The anisotropic displacement exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. H-Atom coordinates ($x10^4$) and isotropic displacement coefficients ($Å^2 x10^3$)

	x	y	z	U
H(1A)	6287	340	9164	80
H(1B)	6384	468	8062	80
H(2A)	8594	124	7866	80
H(2B)	8513	-524	8880	80
H(3A)	9050	1632	8423	80
H(3B)	8967	985	9437	80
H(4A)	7208	3073	9020	80
H(4B)	6860	2150	9830	80
H(5A)	4824	756	6481	80
H(5B)	4624	1696	5598	80
H(6A)	6355	-564	5541	80
H(6B)	6422	494	4761	80
H(7A)	8421	167	5275	80
H(7B)	7887	-214	6305	80
H(8A)	7293	2233	5469	80
H(8B)	7721	1803	6473	80
H(9A)	2236	3018	6465	80
H(9B)	925	4135	6312	80
H(10A)	30	2152	4920	80
H(10B)	-641	3521	5250	80
H(11A)	1377	1595	6068	80
H(11B)	82	2528	6607	80
H(12A)	857	3958	4132	80
H(12B)	1807	2564	4120	80
H(13A)	1988	4336	8908	80
H(13B)	1449	4303	7964	80
H(14A)	225	3208	8647	80
H(14B)	600	3415	9612	80
H(15A)	1809	1585	9708	80
H(15B)	1359	1357	8778	80
H(16A)	3293	1108	8087	80
H(16B)	3727	1393	9006	80
H(21)	5424	8484	8948	80
H(22)	7528	8019	7730	80
H(23)	8993	5797	8066	80
H(24)	7755	4861	9431	80
H(25)	5585	6530	10008	80
H(31)	487	6958	7041	80
H(32)	1307	8580	6083	80
H(33)	2172	9653	7153	80
H(34)	1913	8661	8787	80
H(35)	897	6947	8709	80