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A $\{[\text{TiCl}_2(\text{isodiCp})]_2(\mu\text{-O})\}$ Dimer and a Twinned Cyclic $[\text{TiCl}(\text{isodiCp})(\mu\text{-O})]_4$ Tetramer

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Abstract

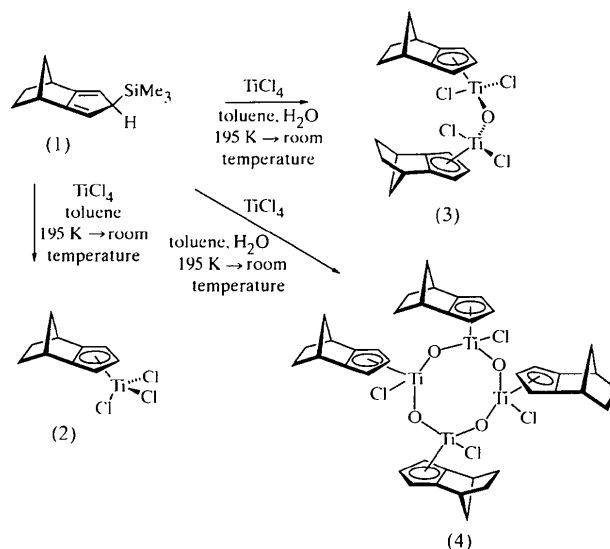
The μ -oxo dimer μ -oxo-bis{dichloro[(1,2,3,3a,7a- η)-4,5,6,7-tetrahydro-4,7-methano-1H-indenyl]titanium}, $[\text{Ti}_2\text{Cl}_4(\mu\text{-O})(\text{C}_{10}\text{H}_{11})_2]$, and the μ -oxo cyclic tetramer, *cyclo-tetra- μ -oxo-tetrakis{chloro[(1,2,3,3a,7a- η)-4,5,6,7-tetrahydro-4,7-methano-1H-indenyl]titanium}*, $[\text{Ti}_4\text{Cl}_4(\mu\text{-O})_4(\text{C}_{10}\text{H}_{11})_4]$, have been synthesized by electrophilic attack of TiCl_4 on the *exo*-trimethylsilyl derivative of isodiCp (isodiCp is the isodicyclopentadienide anion or 4,5,6,7-tetrahydro-4,7-methano-1H-indene) in the presence of trace amounts of moisture. Both structures are *endo* isomers, with each Ti atom bonded in a η^5 manner to the Cp ring of the isodiCp ligand. Both display a slight bending of the isodiCp group about the bond common to the Cp ring and the norbornane fragment, such that the norbornane group is displaced in the direction away from the Ti atom. The dihedral angles which describe this bending are 9.0(3) and 10.2(3) $^\circ$ for the dimer, and 9.2(2) $^\circ$ for the tetramer. The dimer contains a bent Ti—O—Ti angle of 159.5(2) $^\circ$. The tetramer forms tetragonal crystals, which are twinned by merohedry on the (110) plane. The tetramer molecule contains a crystallographic $\bar{4}$ axis, with the Ti atoms linked by the O atoms in a μ -oxo manner to form an eight-membered ring.

Comment

A reliable and useful protocol for controlling the facial selectivity associated with the complexation of transition metals to C_1 -symmetric cyclopentadienyl anions involves prior silylation (Paquette *et al.*, 1983) and chromatographic separation of the silane diastereomers. Subsequent electrophilic attack by the metal reagent proceeds with inversion of configuration (Paquette & Sivik, 1992). Recently, this technique was applied to the completely stereoselective preparation of *endo*- and *exo*-(isodiCp)trichlorotitanium complexes (Gallucci *et al.*, 1997) (isodiCp is the isodicyclopentadienide anion).

The silyl inversion methodology can effectively be used also to generate μ -oxo-(chloro)titanium complexes, thus making available analogs of (2) for direct compari-

son of ligand distortion and ligand orientation. A μ -oxo dimer, (3), and a μ -oxo tetramer, (4), have been synthesized and their structures are reported here. The difference in reaction conditions is subtle, resting on the level of trace amounts of moisture present in the reaction solvent.



The dimer structure, (3), consists of two $\text{TiCl}_2(\text{isodiCp})$ groups bonded together by a μ -oxo bridge (Fig. 1). In the tetramer structure, (4), there is a $\bar{4}$ axis through the center of the molecule, so that the asymmetric unit consists of $\text{TiOCl}(\text{isodiCp})$. The O atoms bond the Ti atoms in a μ -oxo manner to form the cyclic tetramer (Fig. 2). There are two cyclic tetramers in the unit cell. These two structures have features in common with each other and with the *endo*-isomer (2). First of all, the Ti atom is bonded in an *endo* fashion to the isodiCp ligand in all three structures. Each isodiCp moiety is bent slightly about the bond common to the Cp ring and the norbornane fragment [C1—C5 and C11—C15 for (3), and C1—C5 for (4)], and this bending moves the norbornane fragment in the direction away from the Ti atom. The bending can be described by the dihedral angle between the least-squares planes through atoms C1—C5 and through atoms C6, C5, C1 and C9 for one of the isodiCp ligands of (3), as an example. The two dihedral angles for (3) are 9.0(3) and 10.2(3) $^\circ$, while that for (4) is 9.2(2) $^\circ$. These dihedral angles are in the same direction and comparable in magnitude to that of 10.8(2) $^\circ$ observed for (2). The geometry about each Ti atom is approximately tetrahedral, and each Ti is bonded in a η^5 manner to a Cp ring. The Ti—Cp(ring carbon) distances span a wide range for both structures: 2.291(4)–2.458(3) Å for Ti1 and 2.288(4)–2.430(4) Å for Ti2 in (3), and 2.291(3)–2.482(2) Å in (4). The two Ti—ring centroid distances in (3) are 2.051(2) Å for Ti1 and 2.040(2) Å for Ti2. The Ti—ring centroid distance in (4) is slightly longer at 2.066(1) Å.

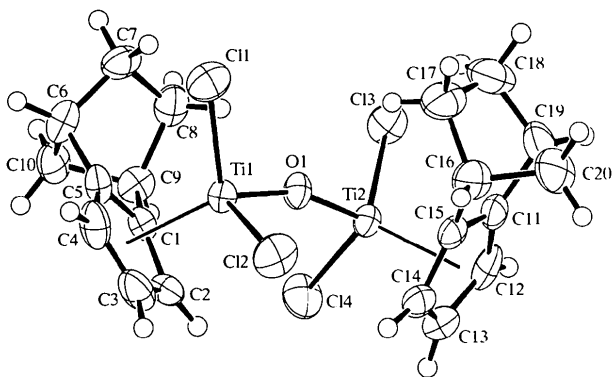


Fig. 1. The molecular structure of (3) drawn with 50% probability displacement ellipsoids for the non-H atoms. H atoms are represented by circles of arbitrary radii.

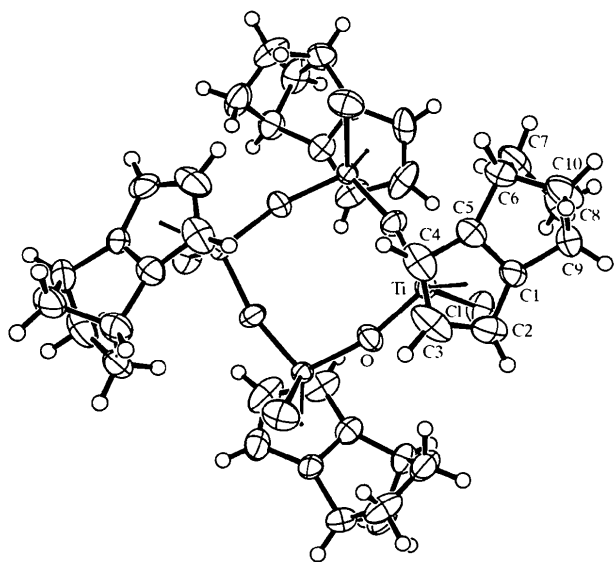


Fig. 2. The molecular structure of (4) drawn with 50% probability displacement ellipsoids for the non-H atoms. H atoms are represented by circles of arbitrary radii.

Close analogs of the dimer (Allegra & Ganis, 1962; Thewalt & Schomburg, 1977; Gowik *et al.*, 1990) have previously been prepared and examined crystallographically. Structure (3) is similar to one of the two crystalline forms of $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2]_2\text{O}$, (5), which have been reported. One form, (5a), contains a Ti—O—Ti angle of 180° and a Ti—O distance of 1.777 (1) Å, with the molecule containing a crystallographic inversion center (Allegra & Ganis, 1962; Thewalt & Schomburg, 1977). The Cp rings are oriented *trans* to each other in (5a) with respect to a view down the Ti—O—Ti axis. The second form, (5b), is comparable to (3) in that it has a bent Ti—O—Ti angle of $167.5(6)^\circ$, and Ti—O bond lengths of 1.801 (9) and 1.809 (9) Å (Gowik *et al.*, 1990). When viewed down the Ti···Ti axis, (3) and (5b) each show a Ti—Cl bond of one Ti atom almost eclipsing a Ti—ring centroid bond of the other Ti atom.

Several μ -oxo tetrameric structures have been reported which are analogs of (4), e.g. $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}(\mu\text{-O})]_4$ [(6); Skapski & Troughton, 1970], $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{TiCl}(\mu\text{-O})]_4$ [(7); Petersen, 1980] and $[(\eta^5\text{-C}_9\text{H}_{11})\text{TiCl}(\mu\text{-O})]_4$ [(8); Samuel *et al.*, 1984]. All of these structures, including (4), can be described in terms of an eight-membered ring of alternating Ti and O atoms, with the Ti atom additionally coordinated to a Cl atom and η^5 coordinated to either a Cp ring or a substituted Cp ring. Structures (4) and (8) each contain a crystallographic $\bar{4}$ axis; their unit cells are metrically similar, but their space groups are different as (8) crystallized in $P\bar{4}2_1c$. While (6) and (7) contain lesser crystallographic symmetry elements, they can also be described in terms of approximate $\bar{4}$ symmetry. In all these structures, the Ti atoms in the ring do not lie in a plane but are arranged in a butterfly conformation. The dihedral angle between two three-atom Ti planes can be used to describe this conformation. For example, in (4), the angle between the plane composed of Ti, Ti² and Ti³, and the plane composed of Ti, Ti³ and Ti⁴ is $157.58(1)^\circ$, where the labeling of the Ti atoms is in a cyclic manner about the ring.

Inspection of the packing arrangement of (4) in the unit cell gave a strong hint for the correct twin law (Fig. 3). The metrical symmetry of the tetragonal cell allows interchange of the *a* and *b* axes, but it is the placement of the molecule within the cell which results in the possibility of twinning. The cell for the minor twin component can easily pack along with the cell for the major twin component without interference from short intermolecular contacts.

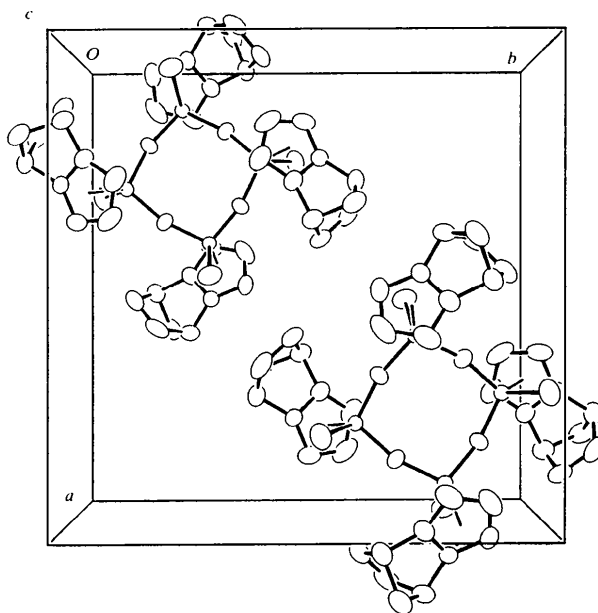


Fig. 3. Unit-cell drawing for the major twin component of (4), viewed down the *c* axis.

Experimental

Compound (3) was synthesized by stirring (1) (4.89 mmol) with TiCl_4 (4.89 mmol) in dried (with KH and CaH_2) toluene (45 ml) for 1 h at 195 K and for 12 h at room temperature. Filtration, solvent evaporation and crystallization from toluene produced red crystals in 48% yield. Compound (4) was synthesized by stirring (1) (6.8 mmol) with TiCl_4 (7.8 mmol) in toluene (75 ml) for 1 h at 195 K and for 10 h at room temperature. Similar work-up of the reaction mixture as with (3) produced orange–yellow crystals in 66% yield.

Compound (3)*Crystal data*[$\text{Ti}_2\text{Cl}_4\text{O}(\text{C}_{10}\text{H}_{11})_2$] $M_r = 515.98$

Monoclinic

 $P2_1/c$ $a = 16.555(1) \text{ \AA}$ $b = 10.062(1) \text{ \AA}$ $c = 12.972(2) \text{ \AA}$ $\beta = 93.153(8)^\circ$ $V = 2157.6(4) \text{ \AA}^3$ $Z = 4$ $D_x = 1.588 \text{ Mg m}^{-3}$ D_m not measured*Data collection*

Rigaku AFC-5S diffractometer

 ω -2 θ scans

Absorption correction:

 ψ scan (North *et al.*, 1968) $T_{\min} = 0.776$, $T_{\max} = 0.861$

5489 measured reflections

4979 independent reflections

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.047$ $wR(F^2) = 0.096$ $S = 1.198$

4977 reflections

244 parameters

H atoms not refined

 $w = 1/[\sigma^2(F_o^2) + (0.0208P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ Table 1. Selected geometric parameters (\AA , $^\circ$) for (3)

Ti1—O1	1.802 (2)	Ti2—O1	1.816 (2)
Ti1—C11	2.2498 (12)	Ti2—C13	2.2429 (12)
Ti1—C12	2.2538 (12)	Ti2—C14	2.2680 (12)
Ti1—C1	2.419 (3)	Ti2—C11	2.430 (4)
Ti1—C2	2.323 (4)	Ti2—C12	2.356 (4)
Ti1—C3	2.291 (4)	Ti2—C13	2.288 (4)
Ti1—C4	2.382 (4)	Ti2—C14	2.328 (4)
Ti1—C5	2.458 (3)	Ti2—C15	2.420 (4)
O1—Ti1—C11	107.74 (9)	O1—Ti2—C14	102.19 (8)
O1—Ti1—C12	100.88 (8)	C13—Ti2—C14	99.64 (5)
C11—Ti1—C12	99.61 (5)	Ti1—O1—Ti2	159.53 (15)
O1—Ti2—C13	106.37 (9)		

Compound (4)*Crystal data*[$\text{Ti}_4\text{Cl}_4\text{O}_4(\text{C}_{10}\text{H}_{11})_4$] $M_r = 922.16$

Tetragonal

 $P4_2/n$ $a = 16.331(1) \text{ \AA}$ $c = 7.498(1) \text{ \AA}$ $V = 1999.7(3) \text{ \AA}^3$ $Z = 2$ $D_x = 1.53 \text{ Mg m}^{-3}$ D_m not measured*Data collection*

Rigaku AFC-5S diffractometer

 ω -2 θ scans

Absorption correction:

 ψ scan (North *et al.*, 1968) $T_{\min} = 0.751$, $T_{\max} = 0.815$

5155 measured reflections

2315 independent reflections

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.026$ $wR(F^2) = 0.073$ $S = 1.176$

2312 reflections

119 parameters

H atoms not refined

 $w = 1/[\sigma^2(F_o^2) + (0.0322P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ Table 2. Selected geometric parameters (\AA , $^\circ$) for (4)

Ti—O'	1.798 (2)	Ti—C2	2.388 (3)
Ti—O	1.802 (2)	Ti—C3	2.291 (3)
Ti—Cl1	2.2758 (7)	Ti—C4	2.322 (2)
Ti—Cl	2.482 (2)	Ti—C5	2.441 (2)
O'—Ti—O	103.60 (11)	O—Ti—Cl1	100.35 (7)
O'—Ti—Cl	103.02 (6)	Ti''—O—Ti	164.25 (12)

Symmetry codes: (i) $y, \frac{1}{2} - x, \frac{1}{2} - z$; (ii) $\frac{1}{2} - y, x, \frac{1}{2} - z$.

In (3), the two Ti-atom positions were located by the Patterson method (SHELXS86; Sheldrick, 1990). The rest of the molecule was obtained by phasing on these two atoms in DIRDIF (Parthasarathi *et al.*, 1983). A linear decay correction was applied to the data (TEXSAN; Molecular Structure Corporation, 1995). Two reflections were omitted from the refinement because of large negative F_o values, *i.e.* (16,7,6) and (12,3,4). For structure (4), the intensity statistics from the $N(Z)$ test appeared non-centrosymmetric (Howells *et al.*, 1950). Since the systematic absences uniquely determined the space group as $P4_2/n$, the structure was solved in this centrosymmetric space group. The setting chosen for this space group places the origin at the inversion center. The Ti atom was located by the Patterson method and the rest of the atoms were obtained by standard Fourier methods. Although the geometry and B values of this model looked reasonable at the isotropic level of refinement, the R value of

Mo $K\alpha$ radiation $\lambda = 0.7093 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 12\text{--}15^\circ$ $\mu = 1.077 \text{ mm}^{-1}$ $T = 296(2) \text{ K}$

Rectangular rod

 $0.35 \times 0.31 \times 0.19 \text{ mm}$

Orange–yellow

1907 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.022$ $\theta_{\text{max}} = 27.5^\circ$ $h = -21 \rightarrow 21$ $k = 0 \rightarrow 21$ $l = 0 \rightarrow 9$

6 standard reflections

every 150 reflections

intensity decay: 5.5%

 $(\Delta/\sigma)_{\text{max}} = -0.213$ $\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

0.25 was too high, and there were many peaks in the difference electron-density map which could not be incorporated into the model. A twin model was then proposed such that the crystal is composed of two twin domains, with the reciprocal lattices of these two components being coincident: $I(hkl) = (1 - \alpha)I(hkl) + \alpha(\bar{k}\bar{h}\bar{l})$. In *SHELXL93* (Sheldrick, 1993), this is incorporated into the least-squares refinement by a twin matrix of (010/100/001) and refinement of the twin fraction α . Application of this twin law resulted in a dramatic drop in the *R* factor to 0.076 [isotropic refinement on $I > 3\sigma(I)$] and a clean difference electron-density map. This is an example of a twin by merohedry with the crystal twinned on the (110) plane. A linear decay correction was applied to the data (*TEXSAN*; Molecular Structure Corporation, 1989). Averaging the symmetry equivalent reflections within the two measured octants, (+*h*, +*k*, +*l*) and (−*h*, +*k*, +*l*), resulted in an *R*_{int} value of 0.022. The twin fraction refined to a value of 0.334 (1). Three reflections were omitted from the refinement because of large negative *F*_o values, i.e. (2, 18, 1), (1, 14, 2) and (11, 17, 1). H atoms for both structures were included in the model at calculated positions using a riding model, with aromatic C—H = 0.93, secondary C—H = 0.97, tertiary C—H = 0.98 Å and *U*_{iso}(H) = 1.2*U*_{eq}(bonded C atom). *PLATON* (Spek, 1990) was used to calculate some metric parameters.

For both compounds, data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995) for (3); *TEXSAN* (Molecular Structure Corporation, 1989) for (4). For both compounds, program(s) used to solve structures: *SHELXS86*; program(s) used to refine structures: *SHELXL93*; molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1123). Services for accessing these data are described at the back of the journal.

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A Trinuclear Molybdenum Cluster Coordinated by *o*-Nitrobenzoate

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Abstract

The title compound, tris(diethyl dithiophosphato)-1 κ^2 S,S';2 κ^2 S,S';3 κ^2 S,S' - μ -*o*-nitrobenzoato-2 κ O:3 κ O'-pyridine-1 κ N- μ_3 -thio-tri- μ -thio-1:2 κ^2 S;1:3 κ^2 S;2:3 κ^2 S-triangulo-trimolybdenum(3 Mo—Mo), [Mo₃S₄(C₇H₄N—O₄)(C₄H₁₀PS₂)₃(C₅H₅N)], was synthesized in a mixed solvent of acetonitrile and ethanol by a ligand-substitution reaction in which *o*-nitrobenzoic acid replaces the bridging diethyl dithiophosphate (DTP) ligand. The average Mo—Mo bond distance is 2.731 (2) Å. The substitution of *o*-nitrobenzoate for DTP shortens the Mo—Mo bond that it bridges to 2.693 (1) Å.

Comment

In the course of our study on the incomplete cubane-type Mo—S(O) cluster compounds, one of the authors proposed that there is quasi-aromaticity in the puckered ring of the Mo₃S₃ moiety (Chen *et al.*, 1990). We were interested in studying the electron delocalization