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Bis(η^5-cyclopentadienyl)bis(methanethiolato)titanium(IV), (η^5-C_5H_5)$_2$Ti(SCH_3)$_2$

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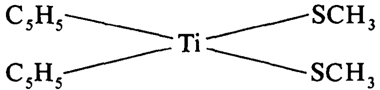
Abstract. M_r = 272·28, tetragonal, $P4_12_12$, a = 9·286 (2), c = 14·489 (4) Å, V = 1249·4 Å^3 at 298 K, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 9·81 cm^{-1}, Z = 4, D_c = 1·447 g cm^{-3}, F(000) = 568. The structure was solved by *MULTAN* and difference electron density syntheses, and refined to R = 0·039 for 1301 reflections. The molecular symmetry is 2 (C_2) with the Ti atoms on the twofold axes. The Ti coordination polyhedron is a distorted tetrahedron formed by the two S atoms of the methanethiolato ligands and the centroids of the cyclopentadienyl rings. The S—Ti—S angle is 93·6 (1)° and the centroid–Ti–centroid angle is 131·4 (1)°. The Ti–S bond length is 2·403 (1) Å and the Ti–centroid distance is 2·069 (3) Å.

Introduction. In a recent study (Dias, Salema & Martinho Simões, 1981; Dias & Martinho Simões, 1982) of the thermochemistry of complexes of the type (η^5-C_5H_5)$_2ML_2$ (M = Mo, W, Ti; L = mono- or polyatomic ligand), a method of evaluation of metal–ligand bond strengths is discussed. This method relies on assumptions that are based on the structural data of the molecules and of the respective ligands. Since the published molecular structures of (η^5-C_5H_5)$_2ML_2$ complexes are insufficient to test the validity of these hypotheses, a study of the title compound, (I), was undertaken to supplement these data.



(I)

Experimental. (η^5-C_5H_5)$_2$Ti(SCH_3)$_2$ was prepared by Clementina Teixeira of the Centro de Quimica Estrutural as described by Giddings (1967). A crystal 0·29 × 0·23 × 0·17 mm was used to collect 1636 *hkl* intensities; 335 $I_o < 3\sigma(I_o)$, θ–2θ scans, θ_{max} = 35°; CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation; no absorption corrections; unit-cell parameters determined from least-squares refinement of $\sin^2\theta$ values for 40 reflections with 17° ≤ θ ≤ 24°; Ti position obtained by direct methods (*MULTAN* 78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), using 250 E values for phase generation; S and C atom positions from subsequent difference Fourier synthesis (*SHELX*; Sheldrick, 1976); full-matrix least-squares refinement, isotropic temperature factors, gave R = 0·084; anisotropic refinement gave R = 0·054; calculated H-atom coordinates refined with isotropic temperature factors (C—H kept fixed at 1·080 Å); $w = K/[\sigma^2(F_o) + |g|F_o^2]$, refined values of K = 1·0211 and g = 0·000467; three strong reflections (110, 012, 022), thought to be suffering from extinction, removed from the data; final R (F) = 0·039, wR (F) = 0·042.

Final difference map revealed no peaks > 0·37 eÅ^{-3}. Atomic scattering factors for Ti, S and C from Doyle & Turner (1968), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections, f' and f'', for Ti from Cromer & Liberman (1970). Atomic coordinates are given in Table 1, selected bond lengths and bond angles in Table 2, and the equations of some planes in Table 3.†

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

x, y, z are ×10^4 for non-hydrogen atoms, ×10^3 for hydrogens. Estimated standard deviations given in parentheses refer to the least significant digit. The equivalent isotropic mean-square coefficient is $B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$. The temperature-factor expression is $T = \exp[-(B\sin^2\theta/\lambda^2)]$.

	x	y	z	B_{eq} or B_{iso}
Ti	−362	−362	0	1·88
S	83 (1)	1698 (1)	963 (1)	2·88
C(1)	143 (5)	3318 (3)	262 (3)	4·42
C(11)	−1244 (4)	−2305 (4)	922 (2)	4·03
C(12)	−539 (3)	−1352 (4)	1515 (2)	3·25
C(13)	940 (3)	−1358 (3)	1281 (2)	3·13
C(14)	1129 (4)	−2302 (3)	537 (2)	3·66
C(15)	−211 (5)	−2859 (3)	305 (2)	4·26
H(1)	54 (4)	421 (3)	67 (2)	5·0
H(2)	−89 (3)	374 (6)	5 (4)	13·0
H(3)	88 (4)	321 (5)	−31 (2)	6·0
H(11)	−236 (1)	−265 (4)	91 (3)	6·4
H(12)	−113 (3)	−71 (3)	201 (2)	3·3
H(13)	177 (3)	−67 (3)	157 (2)	4·2
H(14)	218 (2)	−261 (4)	28 (2)	4·6
H(15)	−36 (4)	−356 (3)	28 (2)	5·3

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† Table 3, and lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38113 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Interatomic distances* (Å) *and angles* (°)

Ti–S	2·403 (1)	S–C(1)	1·816 (3)
Ti–C(11)	2·390 (3)	C(11)–C(12)	1·397 (5)
Ti–C(12)	2·385 (3)	C(12)–C(13)	1·414 (4)
Ti–C(13)	2·401 (3)	C(13)–C(14)	1·402 (4)
Ti–C(14)	2·402 (3)	C(14)–C(15)	1·389 (6)
Ti–C(15)	2·365 (3)	C(15)–C(11)	1·408 (5)
Mean Ti–C	2·389	Mean C–C	1·402
Ti–centroid	2·069 (3)		
Ti–ring normal	2·070 (3)		

S–Ti–S*	93·6 (1)	C(11)–C(12)–C(13)	107·8 (3)
centroid–Ti–centroid*	131·4 (1)	C(12)–C(13)–C(14)	108·0 (3)
S–Ti–centroid	101·4 (1)	C(13)–C(14)–C(15)	107·9 (3)
S–Ti–centroid*	111·4 (1)	C(14)–C(15)–C(11)	108·7 (3)
Ti–S–C(1)	109·9 (1)	C(15)–C(11)–C(12)	107·6 (3)
		Mean C–C–C	108

* Atoms marked with an asterisk are at *y*, *x*, –*z*; *i.e.* the position obtained by the twofold symmetry operation on the same atom at *x*, *y*, *z*.

Discussion. The crystal structure of $(\eta^5\text{-}C_5H_5)_2Ti(SCH_3)_2$ is composed of discrete molecules with the configuration shown in Fig. 1. The metal atom is π-bonded to two cyclopentadienyl ligands and σ-bonded to the S atoms of two methanethiolato ligands. The coordination geometry of the ring centroids and the S atoms about the central Ti atom is a distorted tetrahedron, with twofold axial symmetry through the Ti atom. The planar cyclopentadienyl ligands have a staggered orientation when viewed normal to the twofold axis, as shown in Fig. 2.

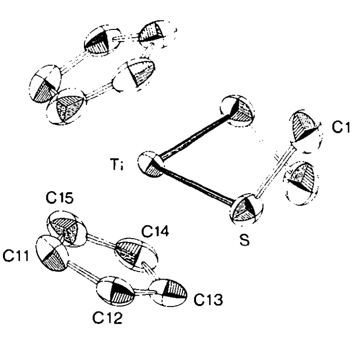

Fig. 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Ti(SCH_3)_2$ with 30% probability thermal ellipsoids (Johnson, 1976). The H atoms are omitted.

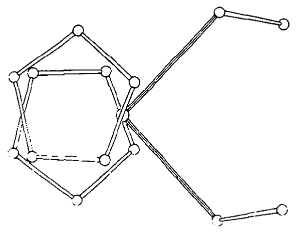

Fig. 2. Projection of the molecule on to the TiS_2 plane.

This study provides an accurate characterization of the $Ti(SCH_3)_2$ fragment. The Ti–S bond length is 2·403 (1) Å, and the S–Ti–S bond angle is 93·6 (1)°. This angle is just on the lower limit of the 94–97° range for the ligand–metal (d^0)–ligand angle which is characteristic of $(\eta^5\text{-}C_5H_5)_2ML_2$ compounds (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The S–Ti–S–C torsion angle is 56·9 (6)°.

When the methanethiolato ligands are substituted by phenylmercapto ligands, as in $(\eta^5\text{-}C_5H_5)_2Ti(SC_6H_5)_2$ (Muller, Watkins & Dahl, 1976), the mean Ti–S bond length of 2·41 Å is comparable to that in this compound, but the (SC_6H_5)–Ti–(SC_6H_5) bond angle is 5·7° greater than the (SCH_3)–Ti–(SCH_3) bond angle. This is expected, since the bulkier (SC_6H_5) ligands should give rise to stronger ligand–ligand repulsions. In $(\eta^5\text{-}C_5H_5)_2TiS_5$ (Muller, Petersen & Dahl, 1976; Epstein & Bernal, 1971) and in $(\eta^5\text{-}C_5H_5)_2Ti(SCH_3)_2Mo(CO)_4$ (Davies & Kilbourn, 1971), the mean Ti–S bond length and the S–Ti–S bond angle are 2·42 Å, 95·0° and 2·435 Å, 94·6° for the two monoclinic forms of the former, and 2·46 Å, 99·9° for the latter.

The skewness of the molecule is indicated by the angle of 7·2° between the plane containing the normals to the cyclopentadienyl ring through the Ti atom and the normal to the plane of the metal and S atoms (Table 3).* This distortion is significant and has been attributed to crystal-packing effects (Prout *et al.*, 1974). In $(\eta^5\text{-}C_5H_5)_2Ti(SC_6H_5)_2$, the angle is 5°, while in several other $(\eta^5\text{-}C_5H_5)_2MLL'$ compounds (Prout *et al.*, 1974; Muller, Petersen & Dahl, 1976), it is close to, or equal to, zero.

The Ti atom is symmetrically bonded to the cyclopentadienyl group as shown by the Ti–C distances given in Table 2. Within experimental error, the metal-to-ring centroid distance of 2·069 (3) Å is equal to the metal-to-ring normal distance of 2·070 (3) Å. The corresponding centroid–Ti–centroid and ring normal–Ti–ring normal angles are 131·4 (1)° and 130·0 (3)°, respectively. This geometry agrees well with that observed in the related compounds shown below:

$(\eta^5\text{-}C_5H_5)_2Ti(SC_6H_5)_2$	2·070 Å and 132·4° (Muller, Watkins & Dahl, 1976)
$(\eta^5\text{-}C_5H_5)_2TiS_5$	2·063 Å and 132·7° (Muller, Petersen & Dahl, 1976)
$(\eta^5\text{-}C_5H_5)_2TiS_5$	2·069 Å and 133·7° (Epstein & Bernal, 1971)
$(\eta^5\text{-}C_5H_5)_2Ti(SCH_3)_2Mo(CO)_4$	2·074 Å and 130·1° (Davies & Kilbourn, 1971)
$(\eta^5\text{-}C_5H_5)_2Ti(C_5H_5)_2$	2·078 Å and 129·9° (Calderon, Cotton, DeBoer & Takats, 1971).

The cyclopentadienyl C atoms are coplanar, with the best plane containing the line defined by C(13) and the middle point between C(11) and C(15). The maximum deviations from that plane are for C(12) and C(14),

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* See previous footnote.

which are ± 0·013 (3) Å from the plane. The intermolecular contacts are normal, except possibly for the shortest, S···H(11) ($-\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{4}-z$) = 2·76 (5) Å. Within experimental error, the cyclopentadienyl ring is equilateral and equiangular, in contrast to that of cyclopentadiene (Damiani, Ferretti & Gallinella (1976).

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Bis(*N*,*N*-dimethylformamide)dinitratodioxouranium(VI), $C_6H_{14}N_4O_{10}U$

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Abstract. $M_r = 540·23$, monoclinic, $P2_1/a$, $a = 16·184\ (2)$, $b = 8·465\ (1)$, $c = 5·6176\ (5)$ Å, $\beta = 101·87\ (1)°$, $V = 753·1\ (1)$ Å^3, $Z = 2$, $D_x = 2·38$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0·71069$ Å, $\mu = 10·263$ mm^{-1}; final $R = 0·028$ for 1188 observed reflexions. The coordination around the U atom is the usual centrosymmetric distorted hexagonal bipyramid.

Introduction. Uranyl complexes with several anionic bidentate ligands and dimethylformamide have been investigated to clarify the relationship between physical properties, structure and the nature of the metal–ligand bonds. Spectroscopic and thermogravimetric experiments are supported by the present crystal structure determination.

Experimental. Yellow prismatic single crystal, 0·10 × 0·10 × 0·15 mm, 2201 independent reflexions to $\theta = 30°$ at 295 K, four-circle diffractometer, $\omega/2\theta$ scan technique, graphite-monochromated Mo $K\alpha$ radiation, no crystal decomposition observed, absorption correction applied with *ORABS* (Schwarzenbach, 1972), absorption factors between 2·19 and 3·21; 1188 reflections observed $[I > 2\sigma(I)]$; scattering factors for neutral atoms and anomalous-dispersion corrections for U from *International Tables for X-ray Crystallography* (1974); structure solved by Patterson method and successive Fourier syntheses; after several cycles of isotropic least-squares refinement with unit weights, a difference synthesis calculated with reflexions within $\sin\theta/\lambda < 0·5$ Å^{-1} showed all H atoms; to prevent bias on $\langle \Delta F\rangle$ *vs* $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$, the last steps of the refinement were performed with weights $w = 1/(a + b|F_o|)^2$, where $a = 2·02$ and $b = 0·24$ for $F_o < 10$, $a = 6·88$ and $b = -0·21$ for $10 < F_o < 27$, $a = 1·20$ and $b = 0·01$ for $F_o > 27$; after weighted refinement

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