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Structural Researches on Organometallic π Complexes: the Crystal and Molecular Structures of Bis-(π-cyclopentadienyl)diisothiocyanatotitanium(IV) and Bis-(π-cyclopentadienyl)maleonitriledithiolatotitanium(IV)

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The crystal and molecular structures of bis-(π-cyclopentadienyl)diisothiocyanatotitanium(IV) [*Imma*, $a=13{\cdot}58$ (1), $b=8{\cdot}14$ (1), $c=11{\cdot}81$ (1) Å, $Z=4$, $R=5{\cdot}8\%$] and bis-(π-cyclopentadienyl)maleonitrile-dithiolatotitanium(IV) [$P2_1/n$, $a=13{\cdot}35$ (1), $b=6{\cdot}88$ (1), $c=15{\cdot}38$ (1) Å, $\beta=105{\cdot}6$ (1)°, $Z=4$, $R=4{\cdot}4\%$] have been determined from three-dimensional X-ray diffractometer data. In these compounds the structures consist of discrete molecules in which two cyclopentadienyls are π-bonded to titanium in a bent arrangement. Coordination is completed by two σ ligands (X). A comparison of the data of the present analyses and those reported in the literature shows that, in the case of chelating ligands, the angle X–M–X is independent of the electron occupancy, but is influenced by the M–X distances and the 'bite' distance. In the isothiocyanato derivative the two cyclopentadienyls have eclipsed conformations; in the maleonitriledithiolato derivative the conformation of the rings is midway (neither staggered nor eclipsed).

Introduction

The chemical bonding in connexion with the molecular structure of bent bis-π-cyclopentadienyl–metal-complexes has recently received much attention. In particular several crystal structure determinations of complexes of this kind have been published by Prout, Cameron, Forder, Critchley, Denton & Rees (1974) [see also Green, Green & Prout (1972)] who propose a new MO-model as an alternative to those previously given by Ballhausen & Dahl (1961) and by Alcock (1967) to justify the observed bond angles formed by the σ-ligands with the metal, and the chemical properties of these compounds.

In the present paper, the crystal and molecular structures of two bent π-cyclopentadienyl–titanium(IV) derivatives are considered: one with the monodentate thiocyanate ligand, bis-(π-cyclopentadienyl)diisothiocyanatotitanium, the other with the bidentate maleonitriledithiolate ligand, bis-(π-cyclopentadienyl)maleonitriledithiolatotitanium. This study was carried out to give more information on the structural aspects of these compounds, particularly examining the effects due to the presence of a bidentate ligand.

Experimental

For both compounds crystal data were determined by Weissenberg and single-crystal diffractometry (Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å). Intensities were measured on an on-line Siemens AED diffractometer (Cu $K\alpha$) using $\omega/2\theta$ scan technique. Data were reduced by Lorentz and polarization factors; no corrections for absorption were made.

The structures were solved by the heavy-atom method starting from three-dimensional Patterson functions. Refinements were carried out by means of least-squares calculations with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were located on final Fourier syntheses and refined isotropically.

The atomic scattering factors used throughout the calculations were those of Cromer & Mann (1968) for Ti, S, N, C, and those of Stewart, Davidson & Simpson (1965) for H.

Table 1. *Bis-(π-cyclopentadienyl)diisothiocyanatotitanium: final atomic fractional coordinates and thermal parameters with their e.s.d.'s in parentheses*

The anisotropic temperature factor is: $\exp[-0{\cdot}25(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$.

	x/a	y/b	z/c	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ti	0	0·2500	0·2064 (2)	1·94 (7)	2·53 (8)	1·74 (6)	0	0	0
S	0·2633 (2)	0·2500	−0·0647 (2)	2·57 (8)	5·34 (11)	3·37 (9)	0	0·89 (7)	0
N	0·1088 (5)	0·2500	0·0896 (6)	3·41 (30)	4·89 (37)	3·70 (32)	0	1·14 (27)	0
C(1)	0·1742 (5)	0·2500	0·0253 (6)	2·80 (30)	3·53 (36)	2·70 (32)	0	0·01 (28)	0
C(2)	0	−0·0373 (13)	0·1787 (10)	12·00 (98)	2·97 (46)	5·75 (61)	0	0	0·06 (42)
C(3)	0·0797 (6)	−0·0029 (10)	0·2419 (8)	6·42 (40)	4·85 (35)	8·01 (47)	2·84 (36)	2·05 (38)	2·54 (38)
C(4)	0·0532 (6)	0·0636 (9)	0·3458 (6)	8·75 (47)	4·66 (33)	5·42 (35)	−0·83 (33)	−4·35 (34)	1·90 (30)
H(2)	0	−0·084 (14)	0·089 (9)	8·5 (3·0)					
H(3)	0·155 (5)	−0·027 (10)	0·216 (6)	8·8 (2·0)					
H(4)	0·098 (5)	0·107 (9)	0·410 (6)	7·5 (1·9)					

Table 2. *Bis-(π-cyclopentadienyl)maleonitriledithiolatotitanium: final atomic fractional coordinates and thermal parameters with their e.s.d.'s in parentheses*

The anisotropic temperature factor is: $\exp\,[-0{\cdot}25(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ti	0·0235 (0)	0·0009 (1)	0·2517 (1)	1·90 (2)	2·99 (2)	1·86 (2)	0·08 (1)	0·74 (1)	−0·10 (1)
S(1)	0·0846 (1)	0·3329 (1)	0·2946 (1)	1·37 (3)	3·00 (3)	2·46 (2)	−0·05 (2)	0·30 (2)	0·30 (2)
S(2)	0·1907 (1)	−0·0810 (1)	0·3561 (1)	2·40 (3)	3·49 (3)	3·15 (3)	0·78 (2)	0·53 (2)	−0·23 (2)
N(1)	0·1572 (3)	0·5509 (5)	0·5251 (2)	6·67 (18)	4·53 (14)	4·34 (14)	0·33 (13)	0·32 (13)	−1·25 (12)
N(2)	0·3079 (3)	0·0532 (5)	0·5952 (2)	4·32 (13)	5·83 (16)	3·38 (11)	0·71 (12)	−0·36 (10)	0·69 (11)
C(1)	0·1469 (2)	0·2812 (4)	0·4064 (2)	2·49 (9)	3·45 (12)	2·60 (10)	−0·32 (9)	0·44 (8)	−0·10 (9)
C(2)	0·1938 (2)	0·1053 (4)	0·4324 (2)	2·10 (9)	3·56 (12)	2·87 (10)	0·10 (9)	0·39 (8)	0·21 (9)
C(3)	0·1530 (3)	0·4296 (5)	0·4723 (2)	3·68 (13)	3·72 (14)	3·10 (11)	0·43 (11)	0·25 (10)	0·13 (10)
C(4)	0·2557 (2)	0·0762 (5)	0·5236 (2)	2·90 (11)	3·92 (13)	3·29 (11)	−0·01 (10)	0·53 (9)	−0·08 (10)
C(11)	−0·0467 (3)	−0·0092 (8)	0·0948 (2)	3·87 (15)	12·09 (36)	1·90 (11)	1·90 (18)	0·36 (10)	−0·96 (15)
C(12)	0·0369 (4)	0·1210 (6)	0·1111 (2)	8·95 (27)	5·02 (18)	2·65 (12)	1·17 (18)	2·58 (14)	0·26 (12)
C(13)	0·1270 (3)	0·0153 (6)	0·1467 (2)	4·74 (16)	6·20 (20)	3·52 (13)	−1·63 (14)	2·51 (13)	−1·07 (13)
C(14)	0·1015 (3)	−0·1763 (5)	0·1540 (2)	4·71 (15)	4·74 (16)	3·77 (13)	0·97 (13)	2·19 (12)	−0·38 (12)
C(15)	−0·0061 (3)	−0·1940 (6)	0·1217 (2)	5·60 (18)	6·75 (22)	3·73 (13)	−2·73 (16)	2·43 (13)	−2·49 (14)
C(21)	−0·1519 (3)	−0·0744 (10)	0·2386 (3)	2·51 (13)	14·93 (44)	4·02 (15)	−2·75 (20)	0·86 (12)	0·81 (22)
C(22)	−0·0933 (4)	−0·2216 (7)	0·2872 (4)	8·00 (26)	4·92 (20)	10·00 (31)	−2·65 (19)	7·04 (26)	−2·08 (20)
C(23)	−0·0384 (3)	−0·1430 (8)	0·3683 (3)	3·44 (14)	10·73 (34)	5·29 (18)	0·96 (18)	2·04 (13)	4·41 (21)
C(24)	−0·0622 (3)	0·0473 (7)	0·3672 (3)	5·20 (18)	8·14 (26)	5·78 (19)	−2·96 (18)	4·16 (17)	−3·13 (19)
C(25)	−0·1313 (3)	0·0911 (7)	0·2868 (4)	4·22 (17)	6·59 (24)	11·94 (36)	2·40 (17)	5·42 (22)	3·65 (24)

Table 2 (*cont.*)

	x/a	y/b	z/c	B
H(11)	−0·120 (4)	0·026 (7)	0·070 (3)	7·7 (1·3)
H(12)	0·036 (4)	0·272 (8)	0·095 (3)	7·9 (1·2)
H(13)	0·204 (4)	0·077 (7)	0·169 (3)	7·2 (1·2)
H(14)	0·153 (3)	−0·292 (7)	0·180 (3)	7·4 (1·2)
H(15)	−0·050 (3)	−0·322 (6)	0·123 (3)	6·1 (1·0)
H(21)	−0·204 (4)	−0·092 (8)	0·181 (3)	9·2 (1·5)
H(22)	−0·088 (4)	−0·361 (7)	0·268 (3)	7·8 (1·2)
H(23)	0·012 (4)	−0·225 (7)	0·423 (3)	7·4 (1·2)
H(24)	−0·034 (4)	0·159 (8)	0·419 (4)	10·3 (1·6)
H(25)	−0·158 (4)	0·234 (10)	0·271 (4)	10·2 (1·6)

All calculations were performed on the CDC 6600 computer of the Centro di Calcolo interuniversitario dell'Italia Nord-Orientale (Bologna).

(1) *Bis-(π-cyclopentadienyl)diisothiocyanatotitanium*(IV)

Orthorhombic dark red prismatic crystals were obtained as described by Giddings (1967). Crystal data are: $(\pi\text{-}C_5H_5)_2Ti(NCS)_2$, $M=294{\cdot}1$, $a=13{\cdot}58$ (1), $b=8{\cdot}14$ (1), $c=11{\cdot}81$ (1) Å, $V=1306$ Å^3, $D_m=1{\cdot}43$, $D_c=1{\cdot}45$ g cm^{-3} for $Z=4$, $F(000)=600$, $\mu=84{\cdot}0$ cm^{-1} (Cu $K\alpha$), space group *Ima*2 or *Imma* (the latter confirmed by structural analysis).

Three-dimensional intensity data were taken at room temperature from a crystal of dimensions $0{\cdot}12\times0{\cdot}14\times0{\cdot}22$ mm mounted around its elongation (b axis). A total of 695 independent reflexions were measured ($6°\le2\theta\le140°$) and 635 having $I>2\sigma(I)$ were used in the crystal analysis. The refinement was carried out by means of full-matrix least squares, minimizing the function $\sum w|\Delta F|^2$ with unit weights. The final conventional R value is 5·8%.

(2) *Bis-(π-cyclopentadienyl)maleonitriledithiolatotitanium*(IV)

The compound was prepared following Locke & McCleverty (1966). Monoclinic dark green crystals suitable for X-ray analysis were obtained by recrystallization from acetone–methanol. Crystal data are: $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$, $M=318{\cdot}2$, $a=13{\cdot}35$ (1), $b=6{\cdot}88$ (1), $c=15{\cdot}38$ (1) Å, $\beta=105{\cdot}6$ (1)°, $V=1360$ Å^3, $D_m=1{\cdot}54$, $D_c=1{\cdot}55$ g cm^{-3} for $Z=4$, $F(000)=648$, $\mu=81{\cdot}2$ cm^{-1} (Cu $K\alpha$), space group $P2_1/n$.

A prismatic crystal ($0{\cdot}11\times0{\cdot}16\times0{\cdot}27$ mm) was mounted around its elongation (b axis) and the intensities of 2587 independent reflexions were measured ($6°\le2\theta\le140°$); 2233 of them with $I>2\sigma(I)$ were used in the analysis.

The structure was refined by means of block-diagonal least squares minimizing the function $\sum w|\Delta F|^2$ at first with unit weights, then applying the weighting scheme proposed by Cruickshank (1965): $w^{-1}=A+B|F_o|+C|F_o|^2$ with $A=0{\cdot}2084$, $B=0{\cdot}03424$, $C=0{\cdot}001406$, deduced from the $\langle|\Delta F|\rangle$ *vs.* $|F|$ distribution (Stout & Jensen, 1968). The final conventional R value is 4·4%.

Results

The final positions and thermal parameters for atoms are quoted in Tables 1 and 2.* Copies of the tables of observed and calculated structure factors are available from the authors on request. The most relevant bond distances and angles and equations for molecular planes are given in Tables 3 to 5. All the average values have been calculated using the formulae:

$$\mu_{\rm av}=\sum_i\frac{\mu_i}{\sigma_i^2}\Big/\sum_i\frac{1}{\sigma_i^2}\,,\quad \sigma_{\rm av}=\sqrt{\frac{1}{\sum_i\frac{1}{\sigma_i^2}}}$$

where μ_i are the individual observations and σ_i are the standard deviations for them.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31338 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The molecular structures of $Cp_2Ti(NCS)_2$ and $Cp_2TiS_2C_2(CN)_2$ are shown in Figs. 1 and 2 respectively. Both compounds consist of monomeric units in which two cyclopentadienyl ligands are π-bonded to titanium in a bent arrangement and the group of atoms TiX_2 ($X = \sigma$-bonded ligand atoms) lies in a plane

Table 3. *Bis-(π-cyclopentadienyl)diisothiocyanatotitanium: interatomic distances and bond angles*

Ti–C(2)	2·361 (11) Å	C(2)–C(3)	1·34 (1) Å	C(2)–H(2)	1·13 (11) Å
Ti–C(3)	2·363 (8)	C(3)–C(4)	1·39 (1)	C(3)–H(3)	1·09 (7)
Ti–C(4)	2·353 (8)	C(4)–C′(4)	1·45 (2)	C(4)–H(4)	1·03 (7)
Average	2·358 (4)	Average	1·370 (5)	Average	1·07 (3)

C(2)–Ti–C(3)	33·1 (3)°	C(2)–C(3)–C(4)	111·3 (8)°
C(3)–Ti–C(4)	34·2 (3)	C(3)–C(4)–C′(4)	105·0 (7)
C(4)–Ti–C′(4)	35·8 (3)	C(3)–C(2)–C′(3)	107·3 (1·0)
Average	34·4 (1)	Average	107·7 (3)
Ti–N	2·021 (7) Å	N–Ti—N′	93·9 (3)°
N–C(1)	1·17 (1)	Ti–N—C(1)	177·5 (6)
S—C(1)	1·611 (7)	N–C(1)–S	179·2 (7)

Table 4. *Bis-(π-cyclopentadienyl)maleonitriledithiolatotitanium: interatomic distances and bond angles*

Ti–C(11)	2·343 (4)	[2·385 (3)] Å *	Ti–C(21)	2·353 (5) Å
Ti–C(12)	2·366 (4)	[2·402 (4)]	Ti–C(22)	2·352 (6)
Ti–C(13)	2·393 (5)	[2·419 (4)]	Ti–C(23)	2·356 (6)
Ti–C(14)	2·381 (4)	[2·403 (4)]	Ti–C(24)	2·379 (6)
Ti–C(15)	2·351 (4)	[2·383 (4)]	Ti–C(25)	2·355(5)
Average	2·365 (2)	[2·397 (1)]	Average	2·358 (2)
C(11)–C(12)	1·400 (7)	[1·446 (7)]	C(21)–C(22)	1·372 (8)
C(12)–C(13)	1·386 (6)	[1·431 (6)]	C(22)–C(23)	1·391 (7)
C(13)–C(14)	1·374 (6)	[1·416 (5)]	C(23)–C(24)	1·358 (8)
C(14)–C(15)	1·393 (6)	[1·441 (6)]	C(24)–C(25)	1·363 (7)
C(15)–C(11)	1·400 (7)	[1·443 (7)]	C(25)–C(21)	1·346 (8)
Average	1·390 (3)	[1·433 (3)]	Average	1·367 (3)
C(11)–H(11)	0·98 (5)		C(21)–H(21)	0·98 (3)
C(12)–H(12)	1·07 (5)		C(22)–H(22)	1·01 (5)
C(13)–H(13)	1·08 (5)		C(23)–H(23)	1·06 (4)
C(14)–H(14)	1·06 (4)		C(24)–H(24)	1·10 (6)
C(15)–H(15)	1·06 (4)		C(25)–H(25)	1·05 (7)
Average	1·05 (2)		Average	1·03 (2)
Ti—S(1)	2·455 (3)		C(1)–C(3)	1·426 (5)
Ti—S(2)	2·439 (3)		C(2)–C(4)	1·438 (4)
S(1)–C(1)	1·734 (4)		C(3)–N(1)	1·155 (5)
S(2)–C(2)	1·731 (4)		C(4)–N(2)	1·145 (4)
C(1)–C(2)	1·372 (4)			
C(11)–Ti–C(12)	34·6 (2)°		C(21)–Ti–C(22)	33·9 (2)°
C(11)–Ti–C(15)	34·7 (2)		C(21)–Ti–C(25)	33·2 (2)
C(12)–Ti–C(13)	33·9 (2)		C(22)–Ti–C(23)	34·4 (2)
C(13)–Ti–C(14)	33·4 (1)		C(23)–Ti–C(24)	33·3 (2)
C(14)–Ti–C(15)	34·2 (1)		C(24)–Ti–C(25)	33·5 (2)
Average	34·0 (1)		Average	33·7 (1)
C(11)–C(12)–C(13)	107·5 (4)		C(21)–C(22)–C(23)	107·6 (5)
C(12)–C(13)–C(14)	109·1 (4)		C(22)–C(23)–C(24)	106·2 (4)
C(13)–C(14)–C(15)	108·0 (3)		C(23)–C(24)–C(25)	109·8 (4)
C(14)–C(15)–C(11)	107·8 (3)		C(24)–C(25)–C(21)	107·5 (4)
C(15)–C(11)–C(12)	107·5 (4)		C(25)–C(21)–C(22)	108·8 (4)
Average	108·0 (2)		Average	108·0 (2)
S(1)–Ti—S(2)	81·9 (1)		S(2)–C(2)–C(4)	117·5 (2)
Ti—S(1)–C(1)	96·4 (1)		C(2)–C(1)–C(3)	119·4 (3)
Ti—S(2)–C(2)	97·2 (1)		C(1)–C(2)–C(4)	120·3 (3)
S(1)–C(1)–C(2)	122·0 (2)		C(1)–C(3)–N(1)	179·3 (4)
S(1)–C(1)–C(3)	118·6 (2)		C(2)–C(4)–N(2)	177·7 (3)
S(2)–C(2)–C(1)	122·0 (2)			

* The values in brackets are corrected for rigid-body libration following Schomaker & Trueblood (1968).

Table 5. *Equations of least-squares planes and distances (Å) from these planes*

Atoms not included in the least-squares plane equations are starred.

Bis-(π-cyclopentadienyl)diisothiocyanatotitanium

π-Cyclopentadienyl ring

$0{\cdot}9196y-0{\cdot}3929z=-1{\cdot}1308$

C(2)	0·023
C(3)	−0·013
C(4)	0·002
*Ti	2·044

Bis-(π-cyclopentadienyl)maleonitriledithiolatotitanium†

π-Cyclopentadienyl ring 1

$0{\cdot}3511X-0{\cdot}1690Y-0{\cdot}9209Z=-1{\cdot}6409$

C(11)	0·002
C(12)	−0·004
C(13)	0·004
C(14)	−0·003
C(15)	0·001
*Ti	−2·049

π-Cyclopentadienyl ring 2

$0{\cdot}8856X+0{\cdot}2176Y-0{\cdot}4103Z=-4{\cdot}2256$

C(21)	−0·006
C(22)	−0·007
C(23)	0·013
C(24)	−0·016
C(25)	0·016
*Ti	2·053

Maleonitriledithiolate

$0{\cdot}9313X+0{\cdot}3350Y-0{\cdot}1431Z=0{\cdot}0587$

S(1)	0·001	*C(3)	0·013
S(2)	−0·001	*C(4)	0·169
C(1)	−0·011	*N(1)	0·030
C(2)	0·011	*N(2)	0·337

† The transformation matrix from monoclinic x,y,z to orthogonal X,Y,Z coordinates is:

$$\begin{pmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{pmatrix}$$

at right angles to that containing the normals to the cyclopentadienyl rings at the metal atom. Considering each of these normals as a coordination site, the coordination polyhedron can be seen as a severely distorted tetrahedron in both compounds. The distortion is indicated by the values of the angles Cp_1–Ti–Cp_2 (133·7° and 130·7° for $Cp_2Ti(NCS)_2$ and $Cp_2TiS_2C_2(CN)_2$ respectively) and X–Ti–X (93·9° and 81·9° for $Cp_2Ti(NCS)_2$ and $Cp_2TiS_2C_2(CN)_2$ respectively.

Crystallographic requirements impose a C_{2v} symmetry for the $Cp_2Ti(NCS)_2$ molecule. The same symmetry approximately holds for the coordination polyhedron in $Cp_2TiS_2C_2(CN)_2$, as the lines bisecting the angles S–Ti–S and Cp_1–Ti–Cp_2 are nearly coincident. For this last compound the symmetry of the molecule as a whole is only C_1, the best plane of the maleonitriledithiolate ligand being tilted by 43° with respect to the TiS_2 plane.

The differences in the titanium–carbon distances (Tables 3 and 4) are small enough to consider a *pentahapto* coordination mode in both compounds. The mean Ti–C values are in agreement with those found in other bis(cyclopentadienyl)titanium complexes, *e.g.* 2·375, 2·398 Å in ethylene-1,2-dithiolato-di-(π-cyclopentadienyl)titanium (Kutoglu, 1973), 2·37 Å in benzene-1,2-dithiolato-di-(π-cyclopentadienyl)titanium (Kutoglu, 1972), 2·374 in di-(π-cyclopentadienyl)titanium pentasulphide (Epstein, Bernal & Köpf, 1971). These distances are influenced by thermal motion or disorder, by which cyclopentadienyls are affected. These effects justify the fact that the carbon–carbon ring distances have values a little lower [mean values: 1·37 Å for $Cp_2Ti(NCS)_2$ and 1·39, 1·37 Å for $Cp_2TiS_2C_2(CN)_2$] than that (1·43 Å) usually accepted for these distances (Wheatley, 1967). Attempts to correct for thermal motion using the Schomaker & Trueblood (1968) treatment succeeded in giving significant results only for one ring, C(11)···C(15), of $Cp_2TiS_2C_2(CN)_2$, for which the corrected mean C_{ring}–C_{ring} distance rises to the expected value of 1·43 Å. For the other rings which are affected by a greater ap-

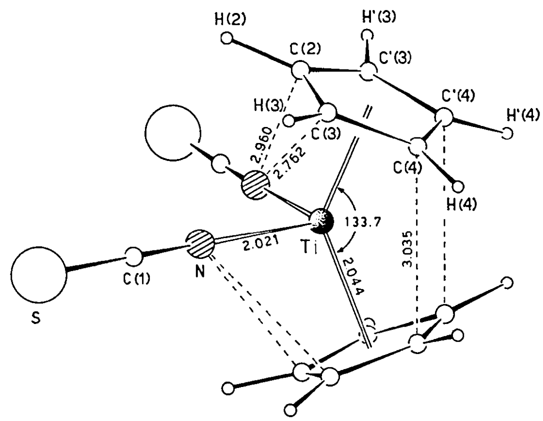

Fig. 1. (π-$C_5H_5)_2Ti(NCS)_2$. Clinographic projection of the molecule.

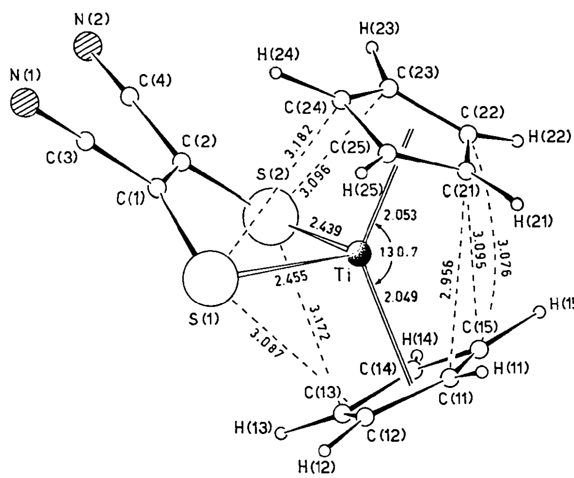

Fig. 2. (π-$C_5H_5)TiS_2C_2(CN)_2$. Clinographic projection of the molecule.

parent thermal motion, no meaningful results were obtained, indicating that they are probably affected by disorder.

The metal-to-ring normal distances [2·04 Å for $Cp_2Ti(NCS)_2$ and 2·05 Å for $Cp_2TiS_2C_2(CN)_2$], which are less affected by thermal motion or disorder than the carbon–metal distances, are in agreement with the values quoted in Table 6 for other Cp_2Ti complexes. This table shows that the X–Ti–X angle considerably decreases in the compounds where the X's belong to chelating five-membered ligands, with respect to the compounds where the X's belong to monodentate ligands. In these last compounds the X–Ti–X angles are close to those found in the series $(\pi\text{-}C_5H_5)_2MX_2$ when the metal is a d^0 system (Green *et al.*, 1972). Considering the compounds with chelating ligands it is found that, when the chelation ring is five-membered, the X–Ti–X angle falls in the range 78–83°, which corresponds to that observed for d^2 systems with monodentate ligands. It is worth observing that the geometry of $Cp_2TiS_2C_2(CN)_2$, in which the 'bite' distance is 3·208 (4) Å, is quite close to that of Cp_2(toluene-3,4-dithiolato)molybdenum where the metal is a d^2 system [Mo–S = 2·433 Å, S–Mo–S = 82·4°, 'bite' distance = 3·21 Å, Knox & Prout (1969)], which indicates that in the case of chelating ligands, the angle X–M–X is independent of the electron occupancy, but is influenced by the M–X distances and the 'bite' distance.

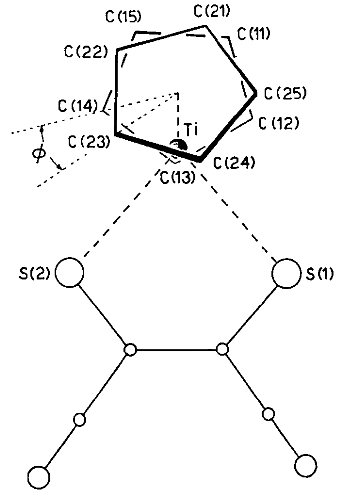

Fig. 3. $(\pi\text{-}C_5H_5)_2TiS_2C_2(CN)_2$. Projection of the molecule onto the plane perpendicular to the ring(centroid)$_1$-Ti-ring(centroid)$_2$ plane.

The cyclopentadienyl rings are planar in both compounds as may be seen from the data quoted in Table 5. Their mutual orientation is eclipsed for symmetry requirements in $Cp_2Ti(NCS)_2$ and intermediate staggered-eclipsed in $Cp_2TiS_2C_2(CN)_2$. To obtain a more accurate description of the conformation of the bis-(cyclopentadienyl) systems the angle φ is considered, formed by a vector running through a vertex and the centroid of one ring and the corresponding vector of the other ring when the rings are projected onto the plane perpendicular to the ring(centroid)$_1$-Ti-ring(centroid)$_2$ plane. This angle, which is 0° or 36° for eclipsed or staggered conformations respectively, assumes a value of 21° in $Cp_2TiS_2C_2(CN)_2$ (Fig. 3). Although the conformations of these systems are mainly determined by crystal packing effects, as indicated by the increase of φ to 33° in the parent compound $Cp_2TiS_2C_2H_2$ (Kutoglu, 1973), intramolecular effects are also important, as can be seen by comparing the ligand–ring and ring–ring contacts in $Cp_2TiS_2C_2(CN)_2$ and in $Cp_2Ti(NCS)_2$ (Figs. 1 and 2). In this last compound the presence of the smaller X ligand atoms allows for the eclipsed conformation with a reduction of the lig and–ring repulsions. This reduction causes an enlarge-

Table 6. *Comparison of some structural parameters for bis-(π-cyclopentadienyl)titanium complexes*

(1) Cp_2TiX_2 complexes with X's belonging to chelating ligands					
Compound	Ti–Cp (Å)	Ti–X (Å)	Cp–Ti–Cp (°)	X–Ti–X (°)	Ref.
$(C_5H_5)_2TiS_2C_2(CN)_2$	2·051 (av)	2·447 (av)	130·7	81·9	*a*
$(C_5H_5)_2TiS_2(C_6H_4)$	2·06 (av)	2·416 (av)	129·9 (av)	82·2 (av)	*b*
$(C_5H_5)_2TiS_2(CH)_2$	2·068 (av)	2·417 (av)	130·9	83·2	*c*
$(C_5H_5)_2Ti(C_6H_4CO_2)$	2·04 (av)	2·20 (Ti–C) 1·95 (Ti–O)	134	78	*d*
$(C_5H_5)_2TiS_4$*	2·068 (av)	2·435 (av)	133·7	94·6	*e*
(2) Cp_2TiX_2 complexes with X's belonging to monodentate ligands					
Compound	Ti–Cp (Å)	Ti–X (Å)	Cp–Ti–Cp (°)	X–Ti–X (°)	
$(C_5H_5)_2Ti(NCS)_2$	2·044	2·021	133·7	93·9	*a*
$(C_5H_5)_2Ti(NCO)_2$	2·055 (av)	2·012 (av)	–	94·7	*f*
$(C_5H_5)_2TiCl_2$	–	2·36 (av)	129·4 (av)	95·2 (av)	*g*
$(C_5H_5)[(CH_3)_5C_5]TiCl_2$	2·07 (av)	2·328 (av)	130	94·8	*h*
$[C_5H_4\text{–}(CH_2)_3\text{–}C_5H_4]TiCl_2$	2·060 (av)	2·368 (av)	132·6	93·7	*i*
$(C_6H_5)_2Ti(C_6H_5)_2$	–	2·27	136	97·3	*j*

* In this compound the large X–Ti–X angle is justified by the presence of a six-membered chelation ring with a 'bite' distance of 3·58 Å.

(*a*) Present work. (*b*) Kutoglu (1972). (*c*) Kutoglu (1973). (*d*) Aleksandrov & Struchkov (1971). (*e*) Epstein, Bernal & Köpf (1971). (*f*) Anderson *et al.* (1974). (*g*) Tkachev & Atomyan (1972). (*h*) Khotsyanova & Kuznetsov (1973). (*i*) Davis & Bernal (1971). (*j*) Kocman, Rucklidge, O'Brien & Santo (1971).

ment of the angle between the normals to the rings and enlargements of the intramolecular distances involving the ends of the rings opposite to the X ligands.

In $Cp_2TiS_2C_2(CN)_2$ the two Ti–S distances [2·455 (3) and 2·439 (3) Å] are not significantly different. Their mean value [2·447 (2) Å] is significantly larger than the values found in ethylene-1,2-dithiolato-di-(π-cyclopentadienyl)titanium [2·417 (1) Å] (Kutoglu, 1973) and benzene-1,2-dithiolato-di-(π-cyclopentadienyl)titanium [2·416 (4) Å] (Kutoglu, 1972). Also the C–C distance in the chelation ring is significantly longer than that of 1·342 (4) Å found in $Cp_2TiS_2C_2H_2$. However, these lengthenings can hardly be justified by the electron-withdrawing character of the CN groups, since the C–C distances involving these groups correspond well to the expected value [1·430 (5) Å] for a single C_{sp^2}–C_{sp} bond (Fritchie, 1966). The S–C distances are not significantly different; they are in the range 1·69–1·77 Å as is reported in the literature for dithiolate ligands and their values indicate some double-bond character. The maleonitriledithiolate ligand is not planar: the group of atoms S(1), S(2), C(1), C(2) lies in a plane, but the two CN groups are significantly out of this plane on the same side (Table 5). Also the metal atom does not lie in that plane which forms a dihedral angle of 41° with the TiS_2 plane.

The structure analysis of $Cp_2Ti(NCS)_2$ confirms that the compound contains *N*-bonded thiocyanate groups, as found on the basis of infrared studies (Burmeister, Deardorff, Jensen & Christiansen, 1970). The Ti–N distance [2·021 (7) Å] is in agreement with those found in the corresponding cyanato complex [2·018 (3), 2·007 (3) Å] (Anderson, Brown & Norbury, 1974). As observed for this last compound, the Ti–N–C–S group is close to linear, the bond angles Ti–N–C(1) and N–C(1)–S being 177·5 (6)° and 179·2 (7)° respectively. Bond distances in the thiocyanate group are in agreement with those usually found in the isothiocyanate complexes (*e.g.* Mokuolu & Speakman, 1975; Cannas, Carta & Marongiu, 1974; Cannas, Carta, Cristini & Marongiu, 1974).

Packing is determined by van der Waals contacts. The intermolecular distances less than 3·5 Å are:

$Cp_2Ti(NCS)_2$

C(2)···C(2^{i})	3·46 (2) Å

i $\bar{x}, \bar{y}-\frac{1}{2}, z$

$Cp_2TiS_2C_2(CN)_2$

C(11)···C(11^{i})	3·468 (6) Å
C(11)···C(12^{i})	3·295 (5)
C(15)···N(2^{ii})	3·449 (6)
C(25)···N(2^{iii})	3·484 (8)

i $\bar{x}, \bar{y}, z$
ii $x-\frac{1}{2}, \bar{y}-\frac{1}{2}, z-\frac{1}{2}$
iii $\bar{x}, \bar{y}, 1-z$

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