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Key indicators

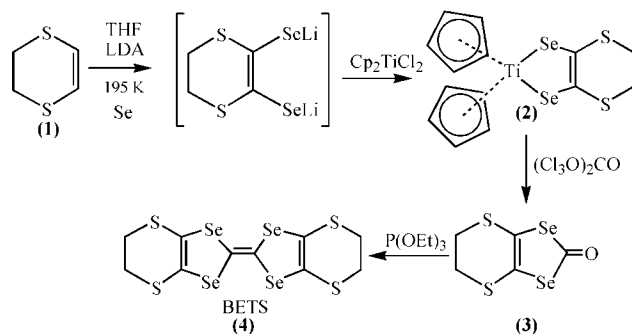
Single-crystal X-ray study
 $T = 180\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$
Disorder in main residue
 R factor = 0.035
 wR factor = 0.097
Data-to-parameter ratio = 12.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**Cp₂Ti(dddse): a well known precursor
for Se-containing donors**

Bis(η^5 -cyclopentadienyl)[5,6-dihydro-1,4-dithiine-2,3-diselenolato(2-)- κ^2 Se,Se']titanium(IV), [Ti(C₅H₅)₂(C₄H₄S₂Se₂)], is isostructural with the all-sulfur derivative Cp₂Ti(ddd) [Guyon *et al.* (1994). *Bull. Soc. Chim. Fr.* **131**, 217–226] [ddd²⁻ = 5,6-dihydro-1,4-dithiine-2,3-dithiolate]. There are two molecules in the asymmetric unit, and one ethylene group of the dddse²⁻ ligand is found to be disordered in one of them. As in Cp₂Ti(ddd), the TiSe₂C₂ ring is folded along the Se...Se axis by 49.75 (3) and 53.29 (3)° in the two independent molecules.

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Comment

The organic donor BETS [bis(ethylenedithio)tetraselenafulvalene], (4), has a central role in interesting conductive and magnetic compounds, exhibiting unusual physical properties (Brossard *et al.*, 1998; Kobayashi *et al.*, 2000; Uji *et al.*, 2001). One of the key steps of the synthesis of BETS (Kato *et al.*, 1991; Courcet *et al.*, 1998) is the isolation of the title compound, (2), which reacts easily with triphosgene to give 4,5-ethylenedithio-1,3-diselenol-2-one, (3). This latter provides BETS, (4), on coupling with triethylphosphite.



We report here the crystal structure of Cp₂Ti(dddse) (ddse is 5,6-dihydro-1,4-dithiine-2,3-diselenolate), and compare it with the sulfur analogue, Cp₂Ti(ddd), whose crystal structure has been reported in 1994 (Guyon *et al.*, 1994). These two compounds are isostructural. The asymmetric unit (Fig. 1) contains two independent Cp₂Ti(dddse) molecules (*A* and *B*) in general positions. The main difference between them is the presence of a disordered terminal ethylene group in molecule *B*. This disorder is probably due to the relative orientation of the *B* molecule with respect to the *A* molecule. Indeed, the —CH₂—CH₂— group of molecule *A* lies between a Cp ring of another molecule *A* and the Se₂C₂S₂ plane of an adjacent *B* molecule (see Fig. 2). Only three short contacts (smaller than the sum of the van der Waals radii; Pauling, 1960) exist between the H atoms of this ethylene group and molecules *A* and *B* (see Table 1), leading to a stable and favourable

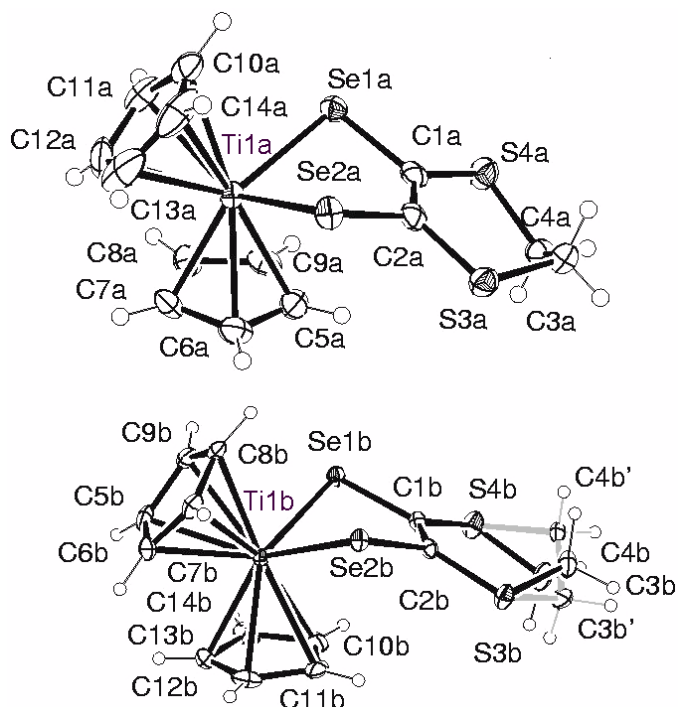


Figure 1

Atomic numbering scheme for the asymmetric unit of $\text{Cp}_2\text{Ti}(\text{dddse})$, with 50% probability displacement ellipsoids; one of the two disordered groups is shown in light grey.

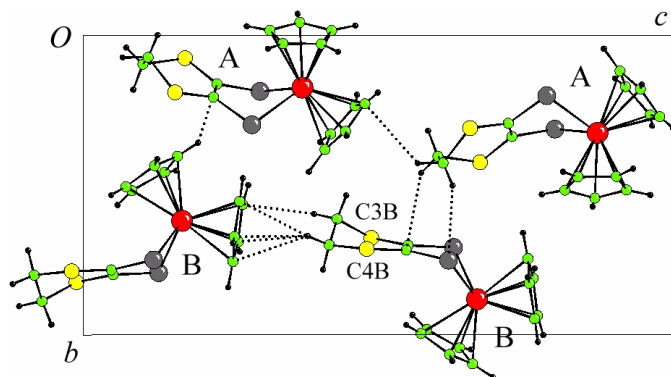


Figure 2

Projection on to the bc plane, showing the short contacts (dotted lines) between the A and B molecules (B is depicted with C3B and C4B as the ethylene group).

conformation. By contrast, the H atoms of the ethylene group of molecule B point directly towards the Cp ring of the closest B molecule (Fig. 2), with six short C...H contacts (Table 1). These contacts are possibly destabilizing. As a consequence, the ethylene group flips to another position (denoted $\text{C3B}'/\text{C4B}'$). This new position of the ethylene group leads also to the occurrence of short contacts with neighbouring A and B molecules (Fig. 3 and Table 1). All of them, but one, also involve contacts with Cp rings. As a consequence, whatever the position, the ethylene groups of the B molecule are always in contact with the Cp rings of the adjacent molecules. In spite of this disorder, both $-\text{CH}_2-\text{CH}_2-$ groups adopts a *trans* configuration, whereas both *trans* and eclipsed configurations

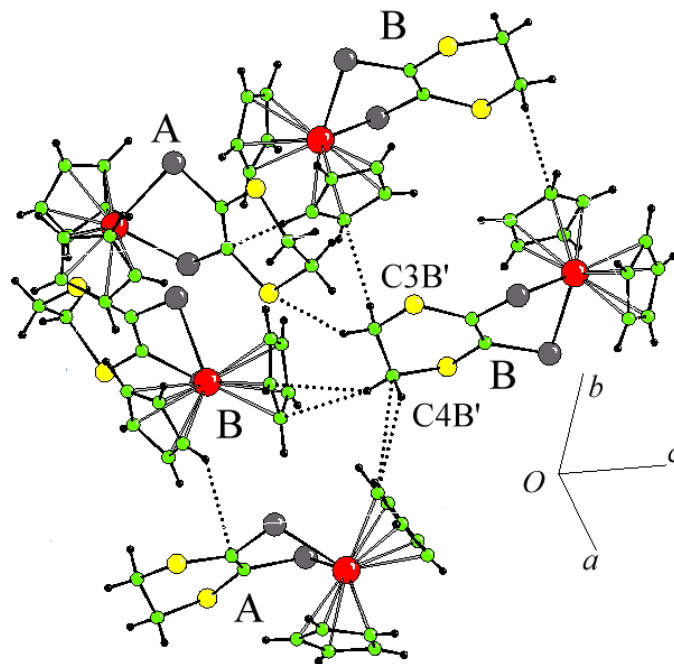


Figure 3

Structure of $\text{Cp}_2\text{Ti}(\text{dddse})$, showing the short contacts between the A and B molecules (B is depicted with $\text{C3B}'$ and $\text{C4B}'$ as the ethylene group).

were reported for $\text{Cp}_2\text{Ti}(\text{dddt})$, without any disorder of the ethylene group. It should be noted here that, in $\text{Cp}_2\text{Ti}(\text{dddt})$, a disorder should also exist in the B molecule, since the equivalent displacement parameters of the C atoms are very large [0.158 (6) and 0.116 (4) \AA^2], and the intramolecular distance between C3B and C4B (1.267 \AA) is too short for a single C—C bond. The presence of this disorder would then 'remove' the eclipsed configuration. As a consequence, $\text{Cp}_2\text{Ti}(\text{dddse})$ and $\text{Cp}_2\text{Ti}(\text{dddt})$ exhibit the same structural features. This is also supported by the folding angle of the TiSe_2C_2 ring along the $\text{Se}\cdots\text{Se}$ line in molecules A and B [49.75 (3) and 53.29 (3)°, respectively]. Substitution of S for Se does not affect the value of the folding angles; these are almost identical in $\text{Cp}_2\text{Ti}(\text{dddt})$ [49.2 (1) and 51.2 (1)°].

Experimental

The title compound was prepared as a powder following the procedure of Kato *et al.* (1991). Dissolution of this powder in CDCl_3 (initially performed for a NMR characterization) and subsequent crystallization afforded crystals suitable for X-ray analysis.

Crystal data

$[\text{Ti}(\text{C}_5\text{H}_5)_2(\text{C}_4\text{H}_4\text{S}_2\text{Se}_2)]$
 $M_r = 452.18$
 Monoclinic, $P2_1/c$
 $a = 12.7474$ (8) \AA
 $b = 10.9055$ (10) \AA
 $c = 21.5888$ (13) \AA
 $\beta = 94.648$ (7)°
 $V = 2991.3$ (4) \AA^3
 $Z = 8$

$D_x = 2.008$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 8000 reflections
 $\theta = 2.8\text{--}26^\circ$
 $\mu = 5.70$ mm^{-1}
 $T = 180$ (2) K
 Plate, dark green
 $0.33 \times 0.25 \times 0.04$ mm

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: analytical
 (Alcock, 1970)
 $T_{\min} = 0.341$, $T_{\max} = 0.765$
 26415 measured reflections
 5732 independent reflections

4603 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\max} = 26.1^\circ$
 $h = -15 \rightarrow 15$
 $k = -13 \rightarrow 13$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.097$
 $S = 1.05$
 5732 reflections
 449 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 4.9237P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.76 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.76 \text{ e } \text{\AA}^{-3}$

Table 1

Short contacts (\AA) between molecules *A* and *B* in $\text{Cp}_2\text{Ti}(\text{dddse})$.

H4B2...C7B ⁱ	2.827 (5)	C1B...H3A1	2.89 (6)
H4B2...C6B ⁱ	2.790 (5)	H3B3...S3A ⁱⁱⁱ	2.921 (1)
H4B2...C5B ⁱ	2.823 (5)	H3B4...C12B ^{iv}	2.659 (6)
H4B2...C8B ⁱ	2.873 (5)	H4B3...C6B ⁱ	2.754 (5)
H4B2...C9B ⁱ	2.8595 (5)	H4B3...C5B ⁱ	2.806 (5)
H3B2...C6B ⁱ	2.900 (5)	H4B4...C14A ⁱⁱ	2.789 (8)
H4A2...C12A ⁱⁱ	2.90 (8)	H4B4...H14A ⁱⁱ	2.3 (1)
Se1B...H4A1	3.05 (7)	C4B'...C14A ⁱⁱ	3.38 (2)

Symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $-x, 1 - y, 1 - z$; (iv) $-x, 2 - y, 1 - z$.

H atoms were found in a difference Fourier map, except those belonging to the disordered ethylene groups of the dddse ligand. These latter were placed geometrically at 0.99 \AA , riding on the carrier C atom, $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the carrier C atom. H atoms on C12A and C13A were also placed geometrically and refined as riding. Other H atoms were refined freely with individual U_{iso} values.

Data collection: *IPDS Software* (Stoe & Cie, 1996); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996) and *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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