Pentachalcogenide Dianions in Transition-metal Complexes: Crystal Structure of Bis-(π-cyclopentadienyl)titanium Pentasulphide

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Summary The anionic pentasulphide chain S_5^{2-} acts as a bidentate ligand to form the "hetero-cyclohexachalcogen" $(C_5H_5)_2TiS_5$: the TiS_5 ring fragment has the chair conformation with Ti–S bond lengths of 2·420 and 2·446 Å and S–S bond lengths which range from 2·051—2·059 Å.

RECENTLY, Köpf[1] reported the synthesis of the series of compounds $(C_5H_5)_2TiS_{5-x}Se_x$ and studied their chemistry, i.r., and n.m.r. spectra. The determination of the crystal structure of $(C_5H_5)_2TiS_5$ has been carried out in order to establish its precise molecular geometry and to determine its relationship to the PtS_{15}^{2-} anion.[2]

Crystal data: monoclinic, $a = 9{\cdot}005(8)$, $b = 13{\cdot}064(11)$, $c = 11{\cdot}284(9)$ Å, $\beta = 93{\cdot}62(1)°$, $D_m = 1{\cdot}70$, $D_c = 1{\cdot}696$ g cm^{-3} for $Z = 4$, space group $P2_1/n$. The intensities of 1479 significant reflections were measured by the θ—2θ scan technique with a Picker four-circle diffractometer equipped with a graphite monochromator and controlled by the Brookhaven Multiple Spectrometer Control System. The phase problem was solved by the heavy-atom method; structural parameters were refined by Fourier and full-matrix least-squares techniques in which the C_5H_5 rings were treated as rigid groups (C–C = 1·42 and C–H = 0·98 Å) while the members of the TiS_5 fragment were treated as individual atoms with anisotropic thermal parameters. At the present stage of refinement $R_1 = 0{\cdot}048$, $R_2 = 0{\cdot}061$.

The molecular configuration of bis-(π-cyclopentadienyl)-titanium pentasulphide is shown in the Figure. At room temperature the TiS_5 ring has a chair conformation which

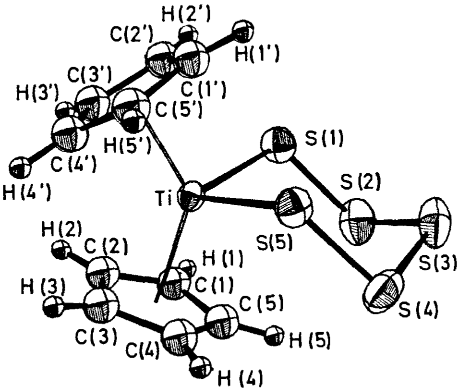

FIGURE. *The chair conformation of the pentasulphide chain leads to asymmetry in the hydrogen–sulphur intramolecular contacts. The shortest contact is between* H(2′) *and* S(1) (2·58 Å).*Contacts ranging from* 2·75—2·89 Å *exist between* H(4) *and* S(5), H(5) *and* S(2), H(1′) *and* S(5), *and* H(5′) *and* S(5). *Intermolecular contacts of about the same length also exist in the lattice.*

results in an asymmetric disposition of the sulphurs with respect to the two C_5H_5 rings. The co-ordination about the titanium atom is that of a distorted tetrahedron: the S(1)–Ti–S(5) angle of 94·6° and the (C_5H_5 centroid)–Ti–(C_5H_5 centroid) angle of 133·6° indicate the extent of this deformation. The Ti–S distances of 2·446 [S(1)] and 2·420 Å [S(5)] and the Ti–(C_5H_5 centroid) distances of 2·062 and 2·067 Å, as well as the angles which involve these positions, agree closely with the corresponding distances and angles in the thio-complex $(C_5H_5)_2Ti(SPh)_2$.[3] The titanium–sulphur geometry in $(C_5H_5)_2TiS_5$ is also similar to the metal–sulphur geometry found in $(NH_4)_2PtS_{15}$.[2] The close agreement of the "bite" of the S_5^{2-} ligand in $(C_5H_5)_2TiS_5$ of 3·58 Å when compared with the non-bonded S–S distance of 3·67 Å in $(C_5H_5)_2Ti(SPh)_2$[3] is of interest since the latter compound does not have the geometrical constraints on the sulphur positions which are imposed in the former compound.

In $(C_5H_5)_2TiS_5$, the Ti–S(1)–S(2) and Ti–S(5)–S(4) angles are 107 and 109°, respectively, while the S–S–S angles range from 103—107°. The four S–S bond lengths range from 2·051—2·059 Å and are in close agreement with the S–S distances in orthorhombic sulphur which range from 2·036—2·043 Å.[4] Such bond lengths imply a certain amount of multiple bond character in the S–S bond (a bond length of 2·05 Å has been estimated[5] to correspond to a bond order of 20%). The invariance of the S–S distances in the TiS_5 fragment suggests that in the complex the two extra electrons are essentially delocalized on the entire TiS_5 moiety.

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