

A structural study on the cubic crystalline modification of $[\text{Cp}_6\text{Ti}_6\text{O}_8][\text{Bu}_3\text{Sn}_3\text{S}_3(\text{SH})_3\text{Cl}]_2$

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Crystal and molecular structures of a cubic crystalline form of $[\text{Cp}_6\text{Ti}_6\text{O}_8][\text{Bu}_3\text{Sn}_3\text{S}_3(\text{SH})_3\text{Cl}]_2$ have been studied by single crystal X-ray diffraction. The cation, $[\text{Cp}_6\text{Ti}_6\text{O}_8]^{2+}$ is a cluster comprising an octahedron with six Ti(IV) atoms at the vertices. Each of the eight faces is capped by an oxygen atom. The cluster is electron deficient as it possesses 84 electrons only. The anion is a six membered ring (with alternated Sn and S atoms) having a chair conformation. The crystal undergoes a phase transition on cooling which has been monitored by X-ray diffraction studies.

Keywords: Organometallic compounds, Organotin compounds, X-ray crystallography, Metal clusters, Cyclopentadienyl compounds, NBO calculations, Phase transitions, Tin, Titanium

Molecular and electronic structures of octahedral metal clusters have been studied for the past several years¹⁻³. The structure of the neutral $\text{Cp}_6\text{Ti}_6\text{O}_8$ cluster has been studied both experimentally (X-ray crystallography)⁴ and theoretically³. As evident from the X-ray study, each Ti atom occupies a vertex of a regular octahedron and is thus bonded to four equivalent Ti neighbors. The total number of electrons required for Cp-Ti and O-Ti bonding in the cluster is 84 while the number of available electrons is 86. Gillespies on the basis of valence-bond arguments, suggested that the two excess electrons located at the centre of the octahedron⁵. Earlier calculations based on extended Hückel approximations also suggested that the two “excess” electrons occupy d_z^2 orbitals from the two Ti atoms which lie along the z coordinate and the $d_{x^2-y^2}$ orbitals from the four Ti atoms lying along x and y coordinates. The coefficients of the orbitals are such that the lobes pointing towards the centre of the octahedron are positive³. In other words, two electrons are present at the centre of the cluster as suggested by the simple valance bond treatment are responsible for holding the

cluster. The presence of two (or more) excess electrons has been observed in all such neutral organotitanium chalcogenide clusters⁶⁻¹⁰.

Very recently, we have synthesized two ionic compounds containing the dicationic cluster $[\text{Cp}_6\text{Ti}_6\text{O}_8]^{2+}$ with the anions either cyclic $[n\text{-Bu}_3\text{Sn}_3\text{S}_3(\text{SH})_3\text{Cl}]^-$ or acyclic $[n\text{-Bu}_3\text{Sn}_3\text{Cl}_3(\text{S})_2(\text{SH})_3]^-$. $[\text{Cp}_6\text{Ti}_6\text{O}_8][n\text{-Bu}_3\text{Sn}_3\text{S}_3(\text{SH})_3\text{Cl}]_2$ crystallizes in two different morphologies (prismatic and star shaped) and have different crystal structures.¹¹ The prismatic crystals are orthorhombic (*Pbca*) while the star shaped crystals have a cubic system with *P2₁3* space group. We report herein the crystal and molecular structure of the cubic crystals.

Experimental

Details of the synthesis of the compound have been reported elsewhere¹¹. X-diffraction analyses were carried out using Xcalibur Eos Oxford CCD diffractometer. The X-ray data were collected at room temperature in the hemisphere mode. Attempts to collect the data at -100 °C were unsuccessful owing to the crystal deformation. It was observed that even at -30 °C there were some changes in the crystal structure. The powder patterns using a single crystal were, therefore, collected at various temperatures. Data integration/reductions were carried out using CrysAlisPro software.¹² Structure was solved by SHELXS-97 and refined using the SHELXL-97 programs¹³ using the WINGX (ver. 1.80.02) platform¹⁴.

Results and discussion

The arrangement of the complex ions in the lattice is shown in Fig. 1. Thermal ellipsoid plot of the cation is shown in Fig. 2a. The six titanium(IV) atoms constitute a perfect octahedron (Fig. 2b) with identical Ti-Ti bonds which is capped by eight oxygen atoms at each of its eight faces. The latter constitute an approximate cube with an O-O distance (edge) varying between 2.453 and 2.498 Å (Fig. 2c). The Ti-O bonds are also identical and their lengths vary between 1.930 and 1.999 Å (Table 1). The small variations in Ti-O bond lengths may be attributed to crystal packing effects. These dimensions are quite comparable to those reported for the orthorhombic form.¹¹

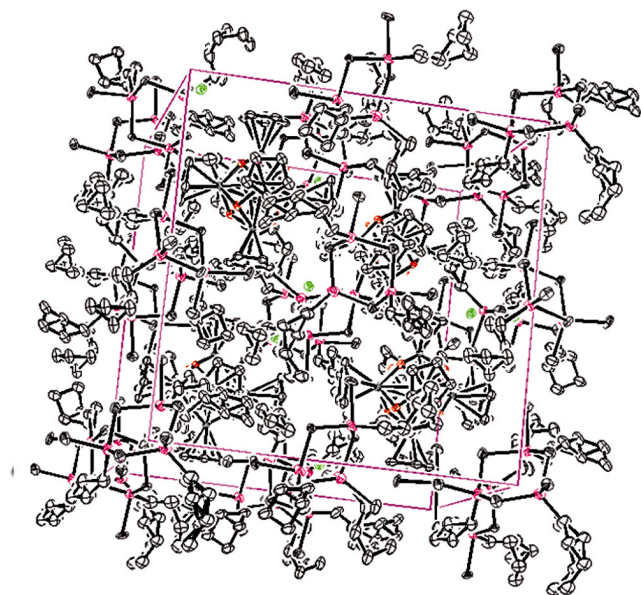


Fig. 1—Arrangement of ions in the unit cell of $[\text{Cp}_6\text{Ti}_6\text{O}_8][\text{Bu}_3\text{Sn}_3\text{S}_3(\text{SH})_3\text{Cl}]_2$.

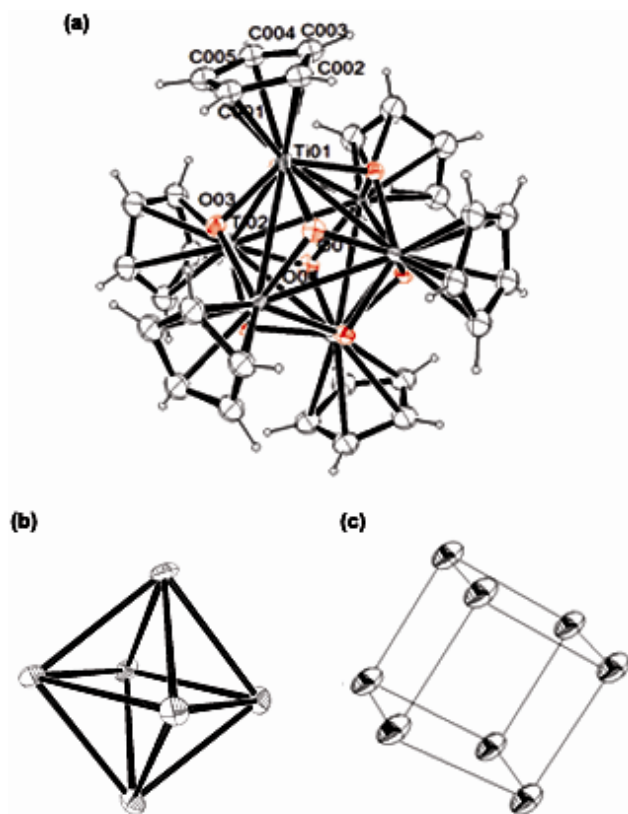


Fig. 2—(a) Structure of the dication $[\text{Cp}_6\text{Ti}_6\text{O}_8]^{2+}$, (b) octahedron constituted by six Ti(IV) atoms and (c) arrangement of the oxygen atoms at the corners of a cube.

The anionic part is also structurally comparable to that of the reported orthorhombic crystal. The three sulphur and three tin atoms constitute a six membered ring with a chair conformation (Fig. 3).

The chlorine atom occupies the axial position of the ring, thus symmetrically capping the three Sn(IV) atoms. The Sn_3S_3 ring is centro-symmetric (Notably, the analogous ring had no centre of symmetry in the case of the orthorhombic crystal). All carbon atoms of the *n*-butyl groups are disordered and each has been refined giving partial occupancies at two different sites. The two Sn-S bond lengths are different, the shorter one being equal to the Sn-SH bond length (Table 1). Six-membered trithia-tritin compounds (R_2SnS_3) are well known and most possess a twisted boat conformation. On the basis of density functional

Table 1—Selected bond lengths and bond angles

Bond lengths ($\text{\AA}$) ^a		Bond angles ($^\circ$) ^a	
Sn-Cl2	2.847(13)	Cl2-Sn -S3	84.6(4)
Sn-S3	2.428(13)	Cl2-Sn -S4	175.4(5)
Sn-S4	2.376(11)	S3 -Sn -S4	94.3(5)
Sn1-S2	2.426(9)	O1 -Ti1-C3	120.9(10)
Sn1-S1	2.334(11)	O3 -Ti1-C3	147.5(10)
Ti1-O2	1.94(2)	O1 -Ti1-C2	89.9(10)
Ti1-O1	2.00(2)	O1 -Ti1-O3	78.7(8)
Ti1-C4	2.30(3)	S1 -Sn1-S2	95.9(4)
Ti1-C1	2.33(3)	Sn -S3 -Sn _a	102.0(5)
Ti1-C2	2.31(3)	O1 -Ti1-O2	129.3(9)
Ti1-O3	1.94(2)		
Ti1-C3	2.30(3)		
Ti1-C5	2.34(3)		

^aEstimated standard deviations in parentheses.

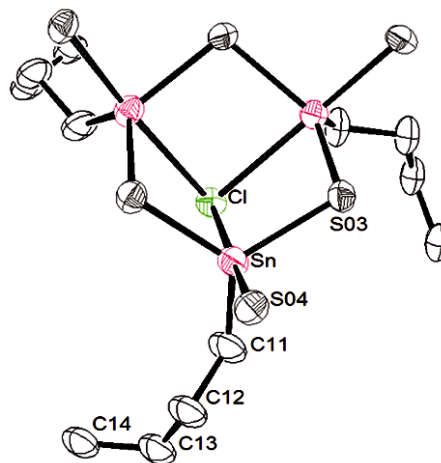


Fig. 3—Structure of the anion $[\text{Bu}_3\text{Sn}_3\text{S}_3(\text{SH})_3\text{Cl}]^{2-}$. [H atoms are omitted for clarity].

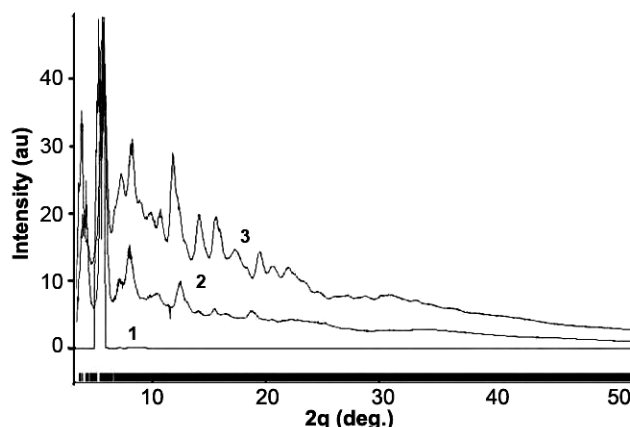


Fig. 4—X-ray diffraction patterns of a crystal of $[\text{Cp}_6\text{Ti}_6\text{O}_8][\text{Bu}_3\text{Sn}_3\text{S}_3(\text{SH})_3\text{Cl}]_2$ at (1) 20 °C, (2) -150 °C and (3) 0 °C (brought back from -150 °C).

calculations, we have shown earlier that the chair conformation is less stable than the twisted boat form as the former suffers from 1,3-diaxial repulsive interactions¹⁵. The anion has chair conformation, as has been recently reported^{16,17} in compounds such as $[(\text{RSn})_3\text{S}_4]^{2-}$. Such a conformation is stabilized possibly because of capping by the Cl atom. It may be mentioned here that organotin hydrosulphides usually undergo condensation reaction leading to the formation of sulphide bridged compounds¹⁸. A few hydrosulphide compounds are, however, known which are stabilized by bulky co-ligands or by rigid frameworks¹⁹. Very recently, we have isolated a triorganotin(IV) hydrosulphide²⁰. In the present case, however, the negative charge prevents the nucleophilic attack of the adjacent SH groups and seems to be the stabilizing factor.

Interestingly, physical properties of the cubic crystals are also different from the orthorhombic crystals. The latter does not show any change in its crystallinity on cooling up to -150 °C while the cubic crystals showed a phase transition below -30 °C. The X-ray diffraction pattern (obtained using a single crystal) of a cubic crystal at room temperature shows a pair of closely spaced peaks at a 2θ values of 3.12 and 3.74 ° (Fig. 4), while at -150 °C the diffraction pattern of the same crystal was quite different showing several other peaks. The crystal exhibited hysteresis when it was brought back to 0 °C (from -150 °C) as all the peaks found at lower temperature were still observable (but less intense). On being brought to room temperature (20 °C) the crystal developed cracks and broke down into very small pieces.

Table 2—Summary of calculated charges on various atoms

Atom	Natural charge	
	Neutral cluster	Dicationic cluster
Ti	+1.71 - +1.77	+1.83
O	-1.01 - -1.02	-1.00
Ghost	-0.09	-0.11

Though the dication possesses 84 electrons and lacks the required 'excess' electrons to hold the cluster intact, yet the Ti-Ti distances indicate the existence of a single bond between each pair of Ti(IV) atoms.²¹ Electronic structure of the cluster dication has been studied on the basis of density functional calculations. The initial coordinates have been obtained from the X-ray data (only $\text{Cp}_6\text{Ti}_6\text{O}_8$ fragment), which were used to fully optimize the structures of both neutral cluster and dicationic cluster using PBE1 hybrid functional^{22,23} and 6-31+G** basis set. The optimized geometries were then used for natural bond orbital (NBO) analyses. A ghost atom designated in Gaussian 03²⁴ was placed at the centre of the octahedron. The natural charges on selected atoms of the neutral and dicationic clusters are listed in Table 2. The idea that the two electrons are located in the centre of the octahedron is not really confirmed by these results. Only a small (natural) charge density could be located at the centre of the octahedron in both neutral and dicationic clusters. The discernible trend from the charge calculation is the increase in negative charge at the centre in the dication with a very small increase in the positive charges on the Ti atoms. As a result, the Ti-Ti distances in the dication is marginally longer than those in the neutral cluster⁴.

Results of second order perturbation theory analysis of Fock matrix in NBO²⁵ basis, however, reveal the nature of bonding in the cluster; the Ti-Ti bonds have formed as a result of donor-acceptor type bond formations between a pair of Ti atoms¹¹.

Supplementary data

Crystallographic data in CIF format (CCDC No. 788690) can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge crystallographic data centre, 12 Union Road, Cambridge CB2 1EZ, UK or by Email: deposit@ccdc.cam.ac.uk.

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