

Tris(thianthrene)(2+) bis(dodecamethylcarba-*closo*-dodecaborate) dichloromethane tetrasolvate: a crossed triple-decker π -trimer dication

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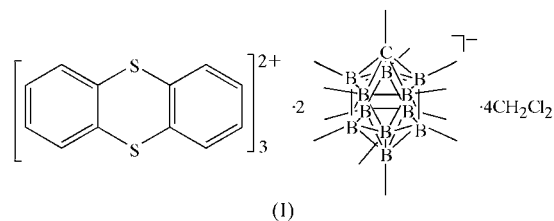
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The title compound, $(3C_{12}H_8S_2)^{2+} \cdot 2C_{13}H_{36}B_{11}^- \cdot 4CH_2Cl_2$, contains an unusual cation–radical association comprising a π -trimer dication of crossed thianthrenes. The thianthrene molecular planes are essentially cofacial, but the S··S axes of adjacent molecules are orthogonal to each other. The outer thianthrenes (both located on mirror planes bisecting the units at the S atoms) are bent slightly towards the inner and planar thianthrene (residing on a $2/m$ symmetry element with the S atoms on the twofold rotation axis), with close noncovalent separations of 3.1 Å indicating strong interplanar interactions within the trimeric dication. Bond-length analysis indicates that the 2+ charge is delocalized over the three stacked thianthrenes with the maximum charge on the central unit. The crossed monomer arrangement is attributed to the frontier-orbital symmetry that allows various π -bonding orientations between thianthrene molecules. The $CB_{11}-(CH_3)_{12}^-$ counter-ion resides on a mirror plane. One of the CH_2Cl_2 solvent molecules resides on a twofold rotation axis, whereas the other is located on a mirror plane.

Comment

The elucidation of the structural features involved in the intermolecular association of planar organic ion radicals is vital to resolving the nature of long-distance π - π intermolecular interactions (Novoa *et al.*, 2001; Lü *et al.*, 2003) and in the development of organic conducting and magnetic materials (Miller, 1983). Thus, according to the maximin principle (Devic *et al.*, 2005), the ion-radical association occurs in a way that simultaneously maximizes the frontier-orbital overlap yet minimizes the interatomic contacts. On the other hand, the packing of some organic ion radicals is found to diverge noticeably in different salts, and such a variability is especially characteristic of the tetrathiafulvalene (TTF) cation radical (Miller, 1983; Rosokha & Kochi, 2007). Thus, in order

to explore the intermolecular association of other S-containing analogues, we examined one of the oldest known cation radicals, thianthrene, in which single-crystal analysis shows the presence of dimeric units with the parallel thianthrenes bent towards each other at a close separation of ~ 3.1 Å between overlapping S atoms (Bock *et al.*, 1994; Nishinaga & Komatsu, 2005). We present here the novel structure of the trimeric thianthrene dication, $[(C_{12}H_8S_2)_3]^{2+}$, displaying a contrasting geometry with an unusual perpendicular arrangement of monomeric units. The latter thus supports the generality of the multivariant orientations observed in TTF and other long-bonded (ion radical) associates.



A dark-violet single-crystal of the title CH_2Cl_2 solvate of the thianthrene dication and the dodecamethylcarba-*closo*-dodecaborate anion, $[(C_{12}H_8S_2)_3]^{2+}[CB_{11}(CH_3)_{12}]^- \cdot 4CH_2Cl_2$, (I), was prepared by slow diffusion of hexane into a CH_2Cl_2 solution containing the cation radical and the neutral thianthrene (see *Experimental*).

The asymmetric unit of (I) (Fig. 1) contains two crystallographically independent thianthrenes, one carborate anion and two CH_2Cl_2 solvent molecules. One of the thianthrenes (located on a $2/m$ symmetry element) is planar, while the molecular plane of the second thianthrene (located on a mirror symmetry element) is essentially parallel to the first, but their S··S axes are orthogonal to one another. One of the

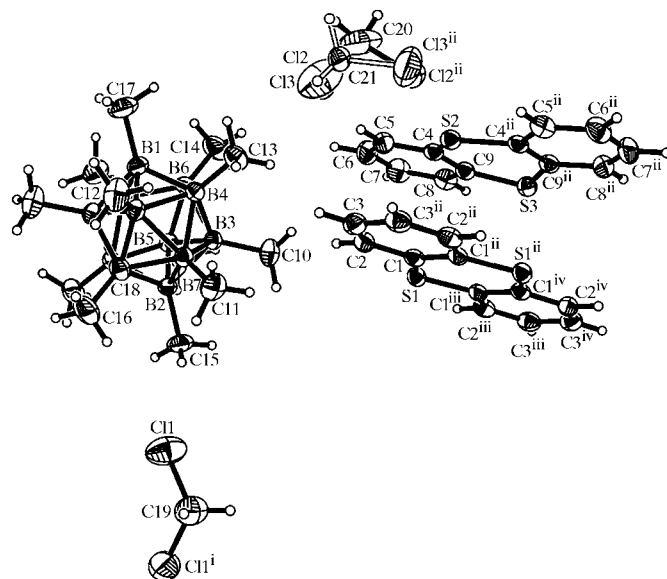


Figure 1

The independent molecular components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, y, -z$; (ii) $x, -y, z$; (iii) $1 - x, y, 1 - z$; (iv) $1 - x, -y, 1 - z$.]

solvent molecules is ordered and resides on a twofold rotation axis, while the other (on a mirror plane) is disordered over two orientations.

The thianthrene molecules form distinct trimeric units (Fig. 2) which are cleanly separated by carbaborate anions and CH_2Cl_2 solvent molecules. In these π -stacked dications, the outer $\text{C}_{12}\text{H}_8\text{S}_2$ units are bent towards the central unit, and the distances between the S atoms and the central plane (3.07 and 3.12 Å for atoms S2 and S3, respectively), as well as the C...S distance of 3.224 (2) Å, are notably contracted compared with the van der Waals contacts of ~ 3.5 Å (Bondi, 1964). Such intermolecular separations are comparable with that observed in the π -dimer formed by the thianthrene cation radical as its AlCl_4^- salt (*ca.* 3.1 Å; Bock *et al.*, 1994), and this indicates the presence of considerable (long-distance) bonding among thianthrene units resulting from the multicentre interaction of the pair of semi-occupied orbitals of the cation radicals with the highest occupied molecular orbital (HOMO) of the neutral $\text{C}_{12}\text{H}_8\text{S}_2$. The bonding interaction is further revealed by the bending of the outer thianthrenes towards the central thianthrene, with dihedral angles between the aromatic planes of $\sim 170^\circ$ (similar to that observed in the dimer). Indeed, since *ab initio* B3LYP/6-311G* computations predict a planar structure for the isolated thianthrene cation radical, such bending (in both the dimeric cations and the outer thianthrenes of the trimer dication) is related to the strong attraction extant between thianthrene moieties, with the charge concentrated primarily on the S-atom centers.

To estimate the overall 2+ charge distribution within the trimer, the bond lengths of the thianthrenes are compared with those in the neutral parent and its cation radical. Indeed, one-electron oxidation of thianthrene to its cation radical is

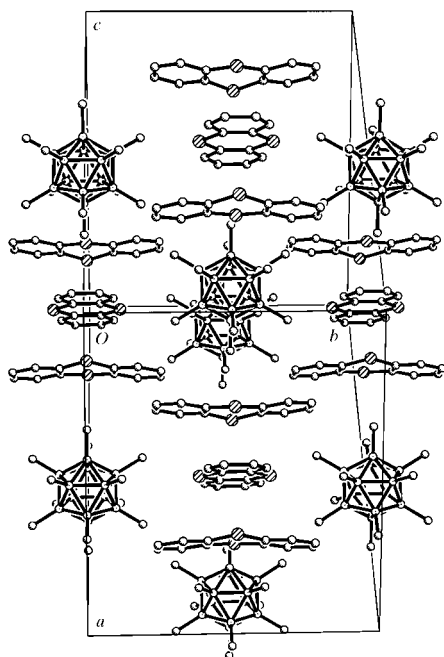


Figure 2

Part of the crystal structure of (I), showing the thianthrene dications separated by the counter-anions. For the sake of clarity, the solvent molecules and the H atoms have been omitted.

accompanied both by the shortening of the S—C bonds from ~ 1.771 (on average) to ~ 1.732 Å and of the outer ($\alpha\beta$) C—C bonds from ~ 1.395 to ~ 1.375 Å, and also by the slight lengthening of the inner and adjacent C—C bonds from ~ 1.395 to ~ 1.41 Å (Larson *et al.*, 1984; Bock *et al.*, 1994). Thus, the geometric characteristics in Table 1 indicate that the bond lengths of the central planar thianthrene unit [*e.g.* C—S bonds of 1.7290 (14) Å and (*ab*) C2—C3 bonds of 1.372 (2) Å] coincide with those of the thianthrene cation radical, indicating the presence of unit charge on this central planar unit. By comparison, the average bond lengths of the two outer thianthrenes in Table 1 (with C—S bonds of 1.736 Å) lie intermediate between the corresponding values in the neutral $\text{C}_{12}\text{H}_8\text{S}_2$ and its cation radical, but much closer to the latter. We thus conclude that the 2+ charge is delocalized over the entire thianthrene trimer assembly, with the maximum found on the central $\text{C}_{12}\text{H}_8\text{S}_2$. This is similar to the TTF trimer reported previously (Triki *et al.*, 1989). Notably, such a charge distribution agrees qualitatively with the $+1/2 + 1/2$ estimate resulting from simple Huckel molecular-orbital computations of electron population in the trimeric system in which four electrons reside on three molecular orbitals resulting from the interaction of the frontier orbitals [two singly occupied molecular orbitals (SOMO) and one HOMO] of two cation radicals and one donor molecule.

The most remarkable feature of the thianthrene trimer, however, is that the S...S axes of neighbouring thianthrenes lie orthogonal, in contrast with their parallel arrangement with overlapping S atoms in the dimeric species, as compared pictorially in Fig. 3. Indeed, both intermolecular associates result from the interaction of the (partially occupied) thianthrene HOMO. However, as illustrated in Fig. 4, the symmetry of this orbital allows the bonding combination to occur with both parallel and perpendicular approaches of the monomers, and these alternatives are observed in both the dimer and the trimer.

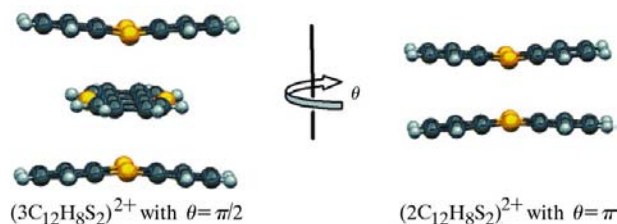


Figure 3

The π -stackings of thianthrene units, showing the mutually crossed arrangement in the trimer (left) and the parallel arrangement in the dimer (right).



Figure 4

The symmetries of the thianthrene HOMOs in the perpendicular (left) and parallel (right) stacking arrangements.

The symmetry of the HOMOs predicts the bonding combination in both the crossed or parallel (overlapped and shifted) TTF cation-radical dimers, as well as in the parallel or perpendicular (to main axis) shifts within tetracyanoquinodimethane (TCNQ) anion-radical dyads, *etc.* (Miller, 1983; Le Magueres *et al.*, 2000; Rosokha & Kochi, 2007). We thus conclude that the multivariance of the ion-radical association, which results in the different bonding combinations of their frontier orbitals, is quite common. Therefore, we believe that the delicate balance between the attractive interactions of partially occupied frontier orbitals *vis-à-vis* the repulsion of filled atomic orbitals is fragile, and it must be explicitly taken into account whenever the maximin principle is invoked. The latter re-emphasizes the possibility that several close potential-energy minima can exist between the various mutual monomer arrangements. Therefore, we postulate that within a narrow range of interplanar separations, the intermolecular interactions can be easily modulated by electrostatics, crystal packing, solvation, *etc.*, to produce a variety of polymolecular associates of the same ion radical with parallel or perpendicular, overlapped or laterally shifted monomer orientations.

Experimental

An aliquot (10 ml) of a 2.5 mM hexane solution of the blue dodecamethylcarboranyl radical [prepared by oxidation of the Cs⁺ salt of the dodecamethylcarba-*closo*-dodecaborate anion, as described previously (King *et al.*, 1996; Rosokha & Kochi, 2006)] was added to a 10 mM solution (5 ml) of thianthrene in CH₂Cl₂. The mixture immediately turned bright violet (the colour characteristic of the thianthrene cation radical) and subsequent cooling to 208 K resulted in the precipitation of a violet powder. The latter was removed by filtration, dried and dissolved in CH₂Cl₂ (5 ml) in a Schlenk tube under an argon atmosphere. The violet solution was layered carefully with a 1:1 CH₂Cl₂-hexane mixture, and then overlaid with pure hexane. The tube was sealed, cooled slowly to 243 K and left undisturbed for 7 d at 243 K, and this led to the formation of dark-violet crystals of (I) suitable for X-ray measurements.

Crystal data

(3C ₁₂ H ₈ S ₂) ²⁺ ·2C ₁₃ H ₃₆ B ₁₁ ⁻ ·4CH ₂ Cl ₂	$\beta = 126.013 (10)^\circ$
$M_r = 1611.27$	$V = 4204 (2) \text{ \AA}^3$
Monoclinic, C2/m	$Z = 2$
$a = 21.585 (8) \text{ \AA}$	Mo K α radiation
$b = 14.573 (4) \text{ \AA}$	$\mu = 0.46 \text{ mm}^{-1}$
$c = 16.523 (5) \text{ \AA}$	$T = 173 (2) \text{ K}$
	$0.5 \times 0.4 \times 0.1 \text{ mm}$

Data collection

Bruker SMART APEX diffractometer	29585 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	6546 independent reflections
$T_{\min} = 0.793$, $T_{\max} = 0.955$	5156 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	272 parameters
$wR(F^2) = 0.139$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$
6546 reflections	$\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$

The molecular-orbital shape of the cation radical SOMO was evaluated using the Cube = (55, orbital) option in single point HF/6-

Table 1

Selected bond lengths (Å).

S1–C1	1.7291 (14)	C4–C5	1.400 (2)
C1–C2	1.4082 (19)	C4–C9	1.4128 (19)
C1–C1 ⁱ	1.413 (3)	C5–C6	1.380 (2)
C2–C3	1.372 (2)	C6–C7	1.392 (2)
C3–C3 ⁱ	1.410 (3)	C7–C8	1.376 (2)
S2–C4	1.7371 (14)	C8–C9	1.410 (2)
S3–C9	1.7344 (15)		

Symmetry code: (i) $x, -y, z$.

311G* computations using the cation-radical geometry optimized via B3LYP/6-311G* computations with GAUSSIAN98 (Frisch *et al.*, 1998). The disordered CH₂Cl₂ solvent has two crystallographically independent C atoms (C20 and C21) and two Cl atoms (Cl2 and Cl3). They were located in a difference Fourier map, with site-occupancy factors of 0.680 (14) and 0.320 (14), respectively, using SHELXTL (Bruker, 2003). The H atoms in the solvent molecules were placed in calculated positions and treated as riding atoms, with C–H = 0.95–0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All other H atoms were treated as riding atoms, with C–H = 0.95–0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT and SADABS (Bruker, 2003); program(s) used to solve structure: SHELXTL (Bruker, 2003); program(s) used to refine structure: SHELXTL; molecular graphics: XP (Bruker, 1999); software used to prepare material for publication: SHELXTL and XCIF (Bruker, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3084). Services for accessing these data are described at the back of the journal.

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