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4,5:4′,5′-Bis(methylenedithio)tetrathiafulvalenium dichloride

Xun-Wen Xiao, Wei Xu,* Hai Xu, De-Qing Zhang and Dao-Ben Zhu*

106 Group, Institute of Chemistry, Chinese Academy of Science, Beijing 100080, People's Republic of China

Correspondence e-mail: wxu@iccas.ac.cn, zhudb@iccas.ac.cn

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.060
wR factor = 0.177
Data-to-parameter ratio = 19.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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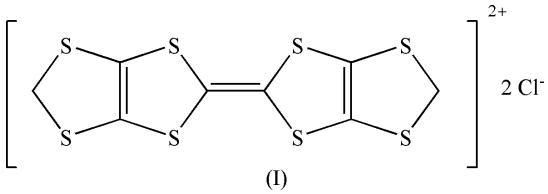
The title compound, $C_8H_4S_8^{2+}\cdot 2Cl^-$, was prepared electrochemically. To our knowledge, it is the first dication salt of tris(methylenedithio)tetrathiafulvalene (BMDT-TTF). The asymmetric unit consists of two chloride anions and one dication, all three located on mirror planes. In the crystal structure, the BMDT-TTF cations form dimers, which are linked by short S···S and S···Cl contacts, leading to a layered structure.

Comment

Studies of radical cation salts of organic electron donors containing tetrathiafulvalene moieties have attracted much interest over the past two decades and more than forty organic superconductors have been reported. Investigation of structure–property relationships is still a main topic in this field. During the search for new molecular conductors, cation-radical salts of TTF-type donors in oxidation states ranging from 0 to +1 have been isolated, but only a few dication salts have been reported. To our knowledge, the only example of a dication salt is BEDT-TTF$(ClO_4)_2$ [BEDTTTF = tris(ethylenedithio)tetrathiafulvalene], which was prepared by electrochemical oxidation in the presence of an oxidizing solvent (Abound *et al.*, 1993). No BMDT-TTF [BMDT-TTF = tris(methylenedithio)tetrathiafulvalene] salts with oxidation states greater than +1 have been reported. We present here the structure of a dication salt of BMDT-TTF, which was synthesized without additional oxidants.



(I)

The asymmetric unit of the title compound consists of two chloride atoms, which are located on a mirror plane, and one dication, which is also located on a mirror plane which passes through atoms C1, C3, C4 and C6 (Fig. 1). The TTF core and the four peripheral S atoms adopt a nearly planar conformation, whereas the two peripheral five-membered rings show a slight envelope conformation. As expected, the C=C bond length of the central double bond of the TTF core [1.420 (8) Å] is longer than in BMDT-TTF monocations. It is known that this bond length is sensitive to the degree of oxidation; this has been frequently used for the estimation of the charge of the donor molecule (Yoneyama *et al.*, 1999; Mas-Torrent *et al.*, 2001).

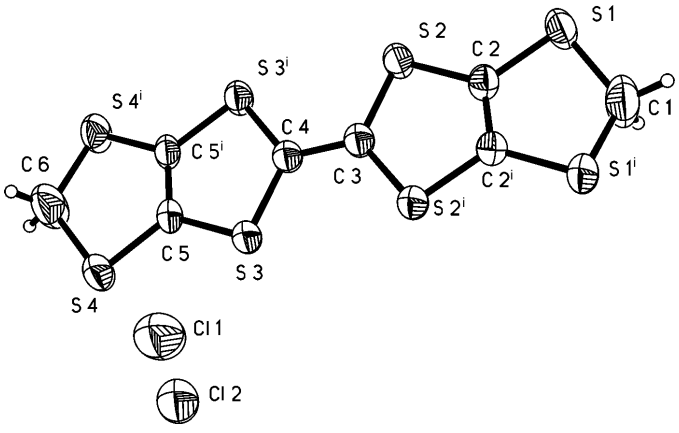


Figure 1
View of the title compound, showing the atom-labeling scheme and displacement ellipsoids at the 50% probability level. [Symmetry code: (i) $x, -y, z$.]

In the crystal structure, the BMDT-TTF cations form dimers with an interplanar distance of 3.373 (7) Å (Fig. 2). This value is very close to that observed in other charge transfer salts of TTF derivatives (Meziere *et al.*, 2000).

These dimers are arranged in layers and no significant π–π interaction is observed between the layers. Within the layers, short intermolecular S···S contacts [shortest = 3.337(2) Å] and S···Cl contacts (range = 3.308–3.443 Å) are observed, which are in the range found in other charge transfer salts (Fig. 3) (Xu *et al.*, 1999).

Experimental

The synthesis of BMDT-TTF was performed as described by Kato *et al.*, 1984). Me_4NCl was purchased from Aldrich chemicals. BMDT-TTF (5 mg) and Me_4NCl (50 mg) were added to freshly distilled CH_3NO_2 (20 ml) and the mixture was stirred for 1 h under an N_2 atmosphere. The solution was then filtered into an electrochemical H-shaped cell. Platinum wires were used as the cathode and anode for the electrocrystallization. Black block-like crystals were obtained at the anode after electrolysis at a constant current of 0.00025 mA for 14 d.

Crystal data

$C_8H_4S_8^{2+}\cdot 2Cl^-$
M_r = 427.49
Monoclinic, $C2/m$
a = 15.405 (3) Å
b = 8.8860 (18) Å
c = 11.105 (2) Å
β = 100.75 (3)°
V = 1493.5 (5) Å^3
Z = 4
D_x = 1.901 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2778 reflections
θ = 2.7–27.5°
μ = 1.53 mm^{-1}
T = 293 (2) K
Block, black
0.30 × 0.20 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
ω scans
Absorption correction: multi-scan (using intensity measurements) (*ABSCOR*; Higashi, 1995)
T_{min} = 0.714, T_{max} = 0.753
2778 measured reflections
1739 independent reflections
893 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 27.5°
$h = -19 \rightarrow 19$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$

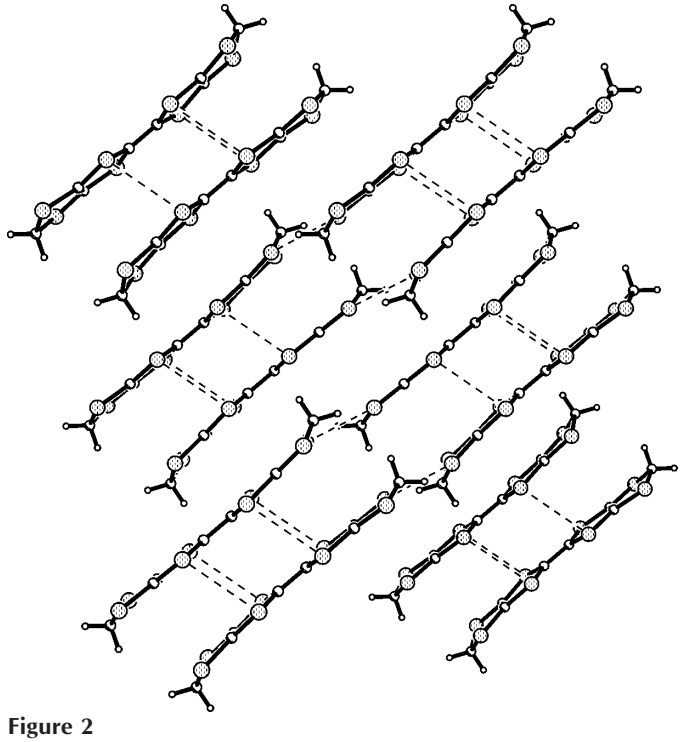


Figure 2
Crystal structure of the title compound, viewed along the b axis, showing the dimers. The dashed lines indicate S···S contacts between the molecules in each dimer.

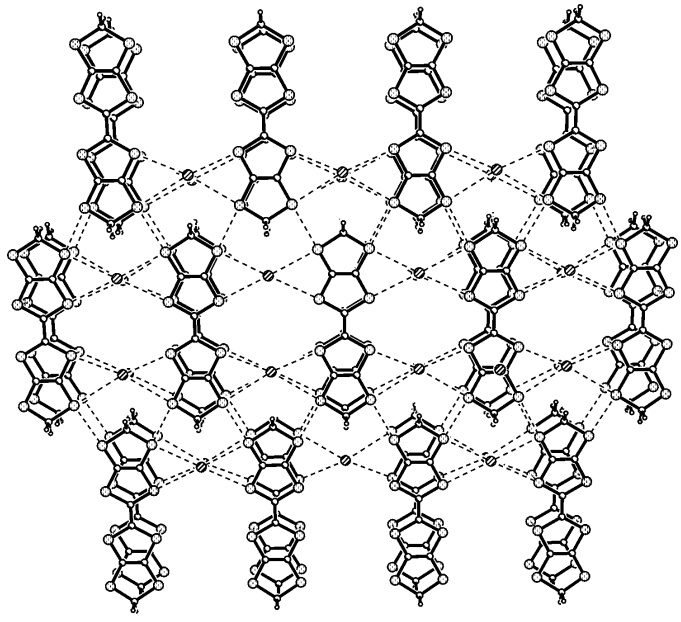


Figure 3
Crystal structure of the title compound, showing the layers. Intermolecular S···S and S···Cl contacts are shown as dashed lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.177
S = 0.93
1739 reflections
91 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.744 (4)	S4—C5	1.739 (4)
S1—C1	1.782 (4)	S4—C6	1.768 (4)
S2—C3	1.730 (3)	C2—C2^{i}	1.372 (9)
S3—C4	1.727 (3)	C3—C4	1.420 (8)
C2—S1—C1	92.5 (3)	C2^{i}—C2—S1	117.76 (14)
C3—S2—C2	93.7 (2)	S1—C2—S2	124.9 (3)
C4—S3—C5	94.0 (2)	C4—C3—S2	121.11 (17)

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

H atoms were positioned with idealized geometry (C—H = 0.97 Å) and refined using a riding model [U_{iso}(H) = 1.2 U_{eq}(C)]. The anisotropic displacement parameters for atoms C1 and C6 are are large, indicating some static or dynamic disorder.

Data collection: *RAPID-AUTO* (Rigaku, 2001); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXTL*.

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