# *X*-Ray Crystal Structure and Properties of Dibenzotetrathiafulvalenium Trichlorodiethylstannate(IV)†

**Gen-etsu Matsubayashi, Ryuichi Shimizu, and Toshio Tanaka***
*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan*

A single-crystal *X*-ray analysis of the salt [dbttf] $[SnEt_2Cl_3]$ has revealed that both the dibenzotetrathiafulvalenium radical cations, $dbttf^{\cdot +}$, and the $[SnEt_2Cl_3]^-$ anions exist as dimers. The crystals are triclinic, space group $P\bar{1}$, with cell dimensions $a = 12.795(3)$, $b = 12.960(5)$, $c = 7.463(1)$ Å, $\alpha = 95.86(3)$, $\beta = 108.62(2)$, $\gamma = 71.44(3)°$, and $Z = 2$. Least-squares refinement, based on 2 459 independent reflections with $|F_o| > 3\sigma(F)$, converged at $R = 0.058$. The electrical resistivity and electronic and e.s.r. spectra of the salt are described.

Organometallic halide anions are of much interest as a counterpart of organic radical cation salts, since the anions may influence the packing modes of the donor molecules. Recently, we reported the novel crystal structures and electrical properties of tetrathiafulvalene (ttf) [2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole] and dibenzotetrathiafulvalene (dbttf) [2-(1′,3′-benzodithiol-2′-ylidene)-1,3-benzodithiole] salts with dialkyltin(IV) chloride anions: $[ttf]_3[SnR_2Cl_4]$ (R = Me[1] or Et[2]), $[ttf][SnMe_2Cl_3]$,[1] and $[dbttf]_3[Sn_3Me_6Cl_8]\cdot PhCN$.[3,4] Diffusion of the $dbttf^{\cdot +}$ radical cation and diethyltin(IV) chloride anions in acetonitrile has yielded the simple $dbttf^{\cdot +}$ radical cation salt $[dbttf][SnEt_2Cl_3]$. This paper reports the crystal structure of this salt as well as its electrical and spectroscopic properties.

## Experimental

*Preparation of* $[dbttf][SnEt_2Cl_3]$.– Diffusion of dbttf[5] (4 mg, 130 µmol)–$[dbttf][BF_4]_{0.8}$[6] (5 mg, 130 µmol) and $SnEt_2Cl_2$ (17 mg, 690 µmol)–$[PPh_3(CH_2Ph)]Cl$ (5 mg, 130 µmol) in acetonitrile (20 $cm^3$) under a nitrogen atmosphere using a convenient U tube[7] for 60 d in a refrigerator gave black plates of $[dbttf][SnEt_2Cl_3]$ (2 mg).

*Physical Measurements.*—The electrical resistivity was measured for a crystal along the *c* axis by the conventional two-probe method, and the powder electronic reflectance and e.s.r. spectra were recorded as described elsewhere.[8]

X-*Ray Crystal Structure of* $[dbttf][SnEt_2Cl_3]$.—Oscillation and Weissenberg photographs indicated a triclinic system and the space group $P\bar{1}$ was confirmed from the successful analysis. Accurate unit-cell parameters were obtained from 25 reflections with 2θ values from 17 to 24°, measured with a Rigaku four-circle diffractometer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University, with Mo-$K_\alpha$ ($\lambda = 0.710\,69$ Å) radiation.

*Crystal data.* $C_{18}H_{18}Cl_3S_4Sn$, $M = 587.63$, triclinic, space group $P\bar{1}$, $a = 12.795(3)$, $b = 12.960(5)$, $c = 7.463(1)$ Å, $\alpha = 95.86(3)$, $\beta = 108.62(2)$, $\gamma = 71.44(3)°$, $U = 1\,111.8(6)$ Å$^3$, $D_m$(flotation) = 1.73 g $cm^{-3}$, $Z = 2$, $D_c = 1.755(1)$ g $cm^{-3}$, $F(000) = 582$, $\mu$(Mo-$K_\alpha$) = 14.7 $cm^{-1}$. Standard cell: $a = 7.463(1)$, $b = 12.795(3)$, $c = 12.960(5)$ Å, $\alpha = 71.44(3)$, $\beta = 84.14(3)$, $\gamma = 71.38(2)°$, transformation matrix 0 0 1, −1 0 0, 0 −1 0.

Intensity data were collected for a specimen, 0.33 × 0.17 × 0.03 mm, by the ω—2θ scan technique up to 50° with a scan rate of 8° $min^{-1}$ in 2θ. No significant intensity variation was observed throughout the data collection. The intensities were corrected for Lorentz and polarization effects, but not for absorption. A total of 4 106 independent reflections was measured, of which 2 459 with $|F_o| > 3\sigma(F)$ were used in the subsequent calculations. The co-ordinates of all the non-hydrogen atoms were obtained by conventional Patterson and Fourier syntheses. A Fourier difference map based on the anisotropic refinement gave the positions of the hydrogen atoms of the benzene ring and of the methylene groups. The methyl hydrogens, however, were omitted from the refinement because their positions were not determined with any certainty. In the final four cycles of block-diagonal least-squares refinement with anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms the residual indices were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.058$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.047$. The weighting scheme $1/w = \sigma^2(F_o) + 0.0001(F_o)^2$ was used. Atomic scattering factors for $Sn^{4+}$, $Cl^-$, and neutral S, C, and H were taken from ref. 9. The final atomic co-ordinates with standard deviations are given in Table 1.

Crystallographic calculations were performed using programs of Professor K. Nakatsu, Kwansei Gakuin University, on an ACOS 900S computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. Figures 1—3 were drawn by the local version of the program ORTEP-II.[10]

## Results and Discussion

A projection of the crystal structure of the salt is given in Figure 1, bond lengths and angles as well as relevant intermolecular atom–atom contacts in Table 2. The crystal structure consists of dimeric units of the $dbttf^{\cdot +}$ radical cations and $[SnEt_2Cl_3]^-$ anions. The geometry of the dimeric anions is illustrated in Figure 2, together with the atom-labelling scheme. The $[SnEt_2Cl_3]^-$ anion assumes a distorted trigonal-bipyramidal geometry around the tin atom with the Sn–C bonds on the equatorial plane, which is essentially the same as for the anions of quinolinium trichlorodimethylstannate(IV)[11] and $[ttf][SnMe_2Cl_3]$.[1] Furthermore, the anions are dimerized through weak contact between the tin and chlorine atoms. Although this is also the case with the above quinolinium salt [Sn ··· Cl 3.367(6) Å][11] and $[ttf][SnMe_2Cl_3]$ [Sn ··· Cl 3.486(7) Å],[1] the present salt exhibits an appreciably weak interaction

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† Dibenzotetrathiafulvalene = 2-(1′,3′-benzodithiol-2′-ylidene)-1,3-benzodithiole.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

**Table 1.** Fractional atomic co-ordinates ( × $10^4$; H, × $10^3$) for [dbttf][$SnEt_2Cl_3$] with estimated standard deviations (e.s.d.s) in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Sn | −1 162.4(7) | 1 908.9(6) | −1 151(1) |
| Cl(1) | −659(2) | 3 555(2) | −469(4) |
| Cl(2) | −3 212(2) | 3 036(2) | −3 357(4) |
| Cl(3) | 888(2) | 925(2) | 1 014(4) |
| S(1) | 5 131(2) | −1 851(2) | 2 741(4) |
| S(2) | 7 159(2) | −1 142(2) | 4 682(4) |
| S(3) | 5 721(2) | 1 287(2) | 3 316(4) |
| S(4) | 3 688(2) | 579(2) | 1 345(4) |
| C(1) | −2 032(10) | 1 753(9) | 777(15) |
| C(2) | −2 561(12) | 2 872(9) | 1 625(17) |
| C(3) | −691(10) | 1 160(9) | −3 612(14) |
| C(4) | 74(13) | 1 772(13) | −4 080(20) |
| C(5) | 6 378(9) | −2 864(8) | 3 881(13) |
| C(6) | 6 429(11) | −3 964(8) | 3 920(16) |
| C(7) | 7 491(11) | −4 707(8) | 4 911(17) |
| C(8) | 8 439(10) | −4 356(8) | 5 808(17) |
| C(9) | 8 394(10) | −3 278(9) | 5 762(15) |
| C(10) | 7 360(9) | −2 526(8) | 4 807(13) |
| C(11) | 5 750(8) | −810(8) | 3 256(13) |
| C(12) | 5 124(8) | 243(7) | 2 675(14) |
| C(13) | 4 506(8) | 2 299(7) | 2 084(14) |
| C(14) | 4 427(10) | 3 381(8) | 2 003(15) |
| C(15) | 3 411(10) | 4 107(8) | 968(16) |
| C(16) | 2 435(10) | 3 773(8) | 6(16) |
| C(17) | 2 485(9) | 2 699(8) | 61(14) |
| C(18) | 3 510(9) | 1 960(8) | 1 097(14) |
| H(6) | 581(11) | −420(9) | 346(17) |
| H(7) | 728(10) | −545(8) | 497(17) |
| H(8) | 922(8) | −488(7) | 639(13) |
| H(9) | 903(8) | −316(7) | 644(12) |
| H(14) | 517(9) | 363(8) | 268(15) |
| H(15) | 327(9) | 488(7) | 83(14) |
| H(16) | 173(12) | 437(10) | −53(19) |
| H(17) | 199(9) | 250(8) | −17(15) |
| H(1-1) | −140(9) | 114(8) | 155(14) |
| H(1-2) | −245(10) | 134(9) | −10(16) |
| H(3-1) | −132(7) | 116(6) | −408(12) |
| H(3-2) | −83(9) | 110(7) | −208(14) |

**Table 2.** Selected distances (Å) and angles (°) for [dbttf][$SnEt_2Cl_3$] with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| Sn–Cl(1) | 2.381(3) | S(3)–C(12) | 1.714(11) |
| Sn–Cl(2) | 2.649(3) | S(3)–C(13) | 1.738(8) |
| Sn–Cl(3) | 2.589(3) | S(4)–C(12) | 1.723(9) |
| Sn–C(1) | 2.139(14) | S(4)–C(18) | 1.752(11) |
| Sn–C(3) | 2.156(11) | C(11)–C(12) | 1.376(12) |
| S(1)–C(5) | 1.738(9) | C(13)–C(18) | 1.432(15) |
| S(1)–C(11) | 1.725(12) | C(1)–C(2) | 1.556(15) |
| S(2)–C(10) | 1.737(11) | C(3)–C(4) | 1.574(25) |
| S(2)–C(11) | 1.715(9) | | |
| S(1) ··· Cl(2′) | 3.445(5) | S(1) ··· S(3′) | 3.389(5) |
| S(2′) ··· Cl(3) | 3.432(4) | S(2) ··· S(4′) | 3.407(5) |
| S(4) ··· Cl(3) | 3.395(4) | Sn ··· Cl(3′) | 3.586(7) |
| Cl(1)–Sn–Cl(2) | 88.59(9) | C(12)–S(3)–C(13) | 96.2(5) |
| Cl(1)–Sn–Cl(3) | 87.5(1) | C(12)–S(4)–C(18) | 96.0(5) |
| Cl(2)–Sn–Cl(3) | 176.0(1) | S(1)–C(11)–S(2) | 116.1(5) |
| Cl(1)–Sn–C(1) | 108.7(3) | S(3)–C(12)–S(4) | 116.9(5) |
| Cl(1)–Sn–C(3) | 109.0(4) | S(1)–C(11)–C(12) | 121.9(8) |
| Cl(2)–Sn–C(1) | 87.2(3) | S(2)–C(11)–C(12) | 121.9(8) |
| Cl(2)–Sn–C(3) | 90.0(3) | S(3)–C(12)–C(11) | 121.6(7) |
| Cl(3)–Sn–C(1) | 94.8(3) | S(4)–C(12)–C(11) | 121.5(8) |
| Cl(3)–Sn–C(3) | 90.6(3) | S(1)–C(5)–C(10) | 116.1(7) |
| C(1)–Sn–C(3) | 142.1(5) | S(2)–C(10)–C(5) | 115.4(6) |
| C(5)–S(1)–C(11) | 95.8(5) | S(3)–C(13)–C(18) | 115.9(7) |
| C(10)–S(2)–C(11) | 96.3(5) | S(4)–C(18)–C(13) | 114.9(6) |

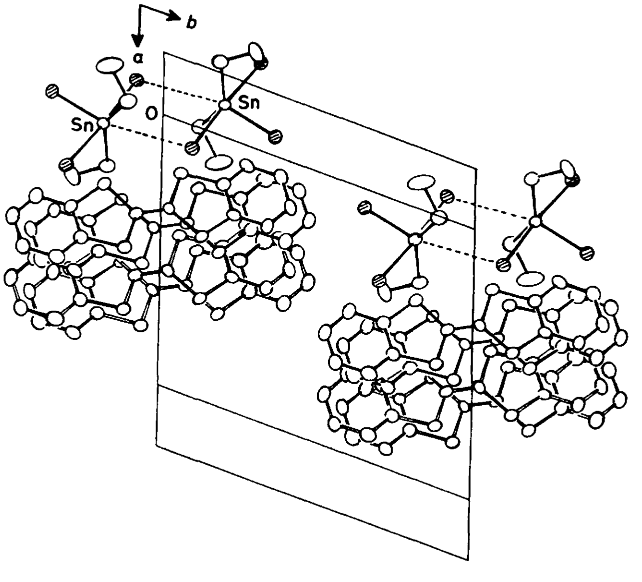

Figure 1. Projection of the crystal structure of [dbttf][$SnEt_2Cl_3$] along the $c^*$ axis

[Sn ··· Cl(3′), Sn′ ··· Cl(3) 3.586(7) Å], nevertheless shorter than the sum of the van der Waals radii of tin and chlorine (4.0 Å).[12] The C–Sn–C angle may be expected to be larger than the regular $sp^2$ angle (120°) owing to the repulsions between the ethyl groups in the equatorial plane and between the ethyl groups and the chlorine atom. Because of the weak Sn ··· Cl(3′) contact in the present salt, the C(1)–Sn–C(3) angle [142.1(5)°] is not so large as C–Sn–C angles in the quinolinium salt [152.2(8)°][11] and in [ttf][$SnMe_2Cl_3$] [154.2(2)°],[1] while it is close to that [140(2)°] in the isolated anion of [$SnMe_2Cl$(terpy)][$SnMe_2Cl_3$] (terpy = 2,2′:6′,2″-terpyridyl).[13]

Figure 3 illustrates the intra- and inter-dimeric molecular overlaps of dbttf$^{\bullet +}$ radical cations. The central C–C distance [C(11)–C(12) 1.376(12) Å] is appreciably larger than that of neutral dbttf [1.336(2),[14] 1.349(6) Å [15]]. Such lengthening has also been reported for [dbttf]$_2$[$Cu_2Cl_6$] [1.404(7) Å],[16] [dbttf]$_2$[$Cu_2Br_6$] [1.397(6) Å],[17] and [dbttf][tftcq] (tftcq = tetrafluorotetracyanoquinodimethane) [1.393(6) Å].[18] In accordance with this, the average C–S distance [C(11)–S(1), C(11)–S(2), C(12)–S(3), C(12)–S(4), 1.719 Å] is less than that (1.758 Å) of neutral dbttf and close to those of [dbttf]$_2$[$Cu_2Cl_6$] (1.719 Å), [dbttf]$_2$[$Cu_2Br_6$] (1.724 Å), and [dbttf][tftcq] (1.718 Å). These results provide evidence in support of the present salt containing the dbttf$^{\bullet +}$ radical cation.

The dbttf$^{\bullet +}$ radical cations are dimerized and almost eclipsed, which is the preferred configuration for the dimer.[18] The average intermolecular spacing within the dimeric unit is 3.42 Å, and the short intermolecular S ··· S contacts are 3.389(5) [S(1) ··· S(3′)] and 3.407(5) Å [S(2) ··· S(4′)]. In accordance with this, the powder electronic reflectance spectrum of the salt exhibits a broad band at 11 800 cm$^{-1}$ assignable to the dbttf$^{\bullet +}$–dbttf$^{\bullet +}$ charge-transfer transition.[4] The salt exhibits three kinds of e.s.r. signals (polycrystalline sample) at 77 K with anisotropic *g* values of $g_{max.}$ = 2.015, $g_{int.}$ = 2.008, and $g_{min.}$ = 2.003, though the signal is somewhat broad at room

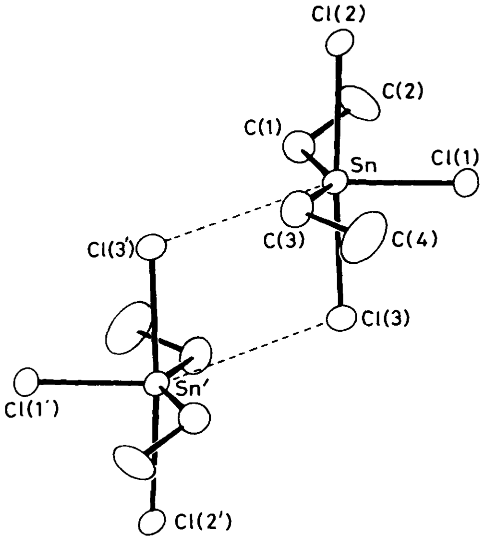

**Figure 2.** Perspective view of the dimeric $[\mathrm{SnEt_2Cl_3}]^-$ anions showing the atom-labelling scheme

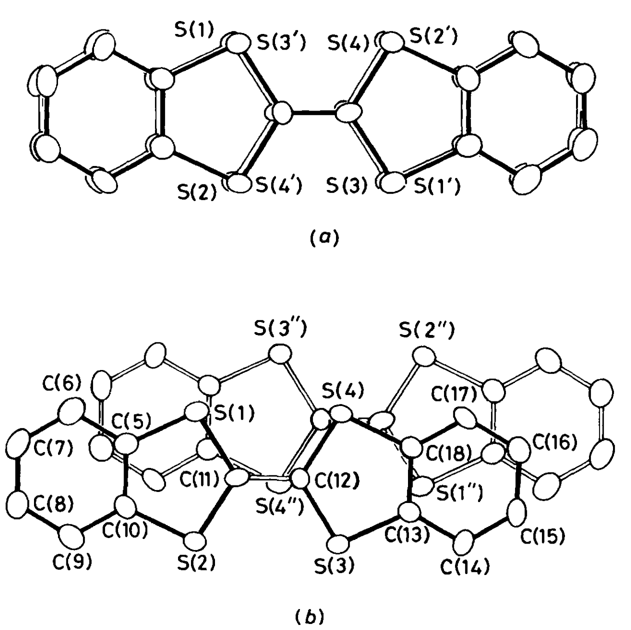

**Figure 3.** Overlapping modes between the dbttf$^{\cdot+}$ radical cations in the intra- (*a*) and inter-dimeric units (*b*), with the atom-labelling scheme

temperature, as shown in Figure 4. Thus, there may be a rather weak spin pairing between the dbttf$^{\cdot+}$ radical cations. Similar e.s.r. signals have been reported for several ttf$^{\cdot+}$ radical cation salts such as $[\mathrm{ttf}]_2[\mathrm{M(C_2O_4)_3}]$ (M = Si or Ge) and $[\mathrm{ttf}]_{2.8}[\mathrm{Sn(C_2O_4)_3}]$.[8]

Although the overlapping between the dimers significantly deviates from the eclipsed mode (Figure 3), the average intermolecular spacing is rather short (3.59 Å). This is consistent with a somewhat small electrical resistivity as a simple salt, $3 \times 10^4\ \Omega$ cm at 25 °C, measured along the *c* axis in the crystal. This finding is in contrast to the presence of isolated dimers in $[\mathrm{ttf}][\mathrm{SnMe_2Cl_3}]$ which exhibits a high resistivity ($1.3 \times 10^7\ \Omega$ cm at 25 °C as a compacted pellet).[1]

The close contacts between the chlorine and sulphur atoms are 3.445(5) [S(1)···Cl(2')], 3.432(4) [S(2')···Cl(3)], and 3.395(4) Å [S(4)···Cl(3)], which are shorter than the sum of van der Waals radii for these atoms (3.65 Å).[12] This is suggestive of an electrostatic interaction between the atoms.

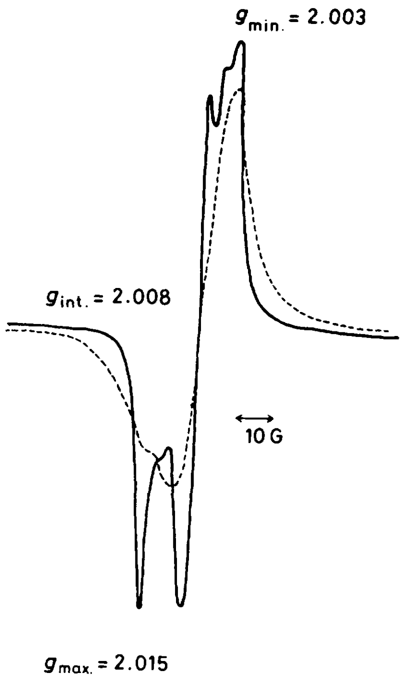

**Figure 4.** Powder e.s.r. spectra of $[\mathrm{dbttf}][\mathrm{SnEt_2Cl_3}]$ at 77 K (——) and at room temperature (– – – –)

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