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CRYSTAL STRUCTURE AND PROPERTIES OF THE DBTTF SALT WITH A NOVEL CHLORIDE-BRIDGED TRIMERIZED DIMETHYLTIN(IV) DIANION. $[DBTTF]_3[Sn_3(CH_3)_6Cl_8]\cdot C_6H_5CN$

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The title salt has been obtained by electrolysis of dibenzotetrathiafulvalene in a benzonitrile solution containing dichlorodimethyltin(IV) and benzyltriphenylphosphonium chloride. The X-ray crystal analysis has revealed the presence of a DBTTF columnar structure and a novel trimerized tin(IV) anion $[Sn_3(CH_3)_6Cl_8]^{2-}$. Electrical and spectroscopic properties also are described.

Organotin(IV) halide anions are of interest as counterparts to prepare electrically conductive radical cation ($D^{\dot{+}}$) salts with new $D^{\dot{+}}$-packings because of some different charges and sizes of these anions.[1,2] Recently, we reported a highly conductive TTF (tetrathiafulvalene) salt with tetrachlorodimethyltin(IV) anion, $[TTF]_3[Sn(CH_3)_2Cl_4]$, which contains a two-dimensional TTF-sheet.[1] In the course of studies in this field, we have obtained the DBTTF (dibenzotetrathiafulvalene) salt with a novel anion, $[DBTTF]_3[Sn_3(CH_3)_6Cl_8]\cdot C_6H_5CN$. This communication describes the crystal structure of this salt as well as its electrical and spectroscopic properties.

DBTTF (50 mg, 0.16 mmol) was electrolyzed under the controlled current (5 μA) in a benzonitrile (10 cm^3) solution containing dichlorodimethyltin(IV) (990 mg, 4.5 mmol) and benzyltriphenylphosphonium chloride (580 mg, 1.5 mmol) for 13 d at room temperature to give black plates (40 mg) of $[DBTTF]_3[Sn_3(CH_3)_6Cl_8]\cdot C_6H_5CN$. Found: C, 38.03; H, 2.85; N, 0.82%. Calcd for $C_{55}H_{53}NCl_8S_{12}Sn_3$: C, 37.83; H, 2.71; N, 0.80%. The structure was determined by a single crystal X-ray analysis. Crystal data: $C_{55}H_{47}NCl_8S_{12}Sn_3$, $\underline{M}$ = 1746.1, triclinic, space group $\underline{P\bar{1}}$, $\underline{a}$ = 12.931(2), $\underline{b}$ = 20.992(4), $\underline{c}$ = 12.485(1) Å, α = 90.07(1), β = 99.18(1), γ =

79.41(1)°, $\underline{U}$ = 3287.4(9) $\mathring{A}^3$, $\underline{Z}$ = 2, $\underline{D}_c$ = 1.7460(5) g cm^{-3}, $\underline{D}_m$(flotation) = 1.75 g cm^{-3}, $\underline{F}$(000) = 1724, μ(Mo-Kα) = 12.2 cm^{-1}. Intensity data (2θ > 55°) were collected on a Rigaku four-circle diffractometer using graphite-monochromated Mo-Kα radiation and an ω-2θ scan technique. Based on 4183 unique observed reflections ($|\underline{F}_o| > 3\sigma(\underline{F})$), the structure was solved by a conventional heavy-atom method and the subsequent Fourier procedure, and refined by the block-diagonal least-squares method with anisotropic thermal vibrations for all non-hydrogen atoms to R = 0.104.

The $[Sn_3(CH_3)_6Cl_8]^{2-}$ anion consists of chloride-bridged trimerized dimethyltin(IV) skeletons (Fig. 1), which is a novel example for chlorodimethyltin(IV) anions in contrast to the fact that TTF salts with trichloro- and tetrachlorodimethyltin(IV) anions are isolated.[1)] For the central tin moiety Sn(2)-Cl distances are 2.66(1) Å (averaged) and the C(3)-Sn(2)-C(4) bond is almost linear (178.3(1)°), while for the terminal tin moieties the Sn(1 and 3)-Cl(terminal) and Sn(1 and 3)-Cl(bridged) distances are 2.44(2) and 3.03(4) Å (averaged), respectively, the C(1)-Sn(1)-C(2) and C(5)-Sn(3)-C(6) bonds being appreciably bent (161.5(2) and 158.6(2)°). Thus, the anion corresponds to the tetrachlorodimethyltin(IV) anion associated with two dichlorodimethyltin(IV) molecules. In the DBTTF salt, the closest contact between the tin(IV) anion-chlorine and DBTTF-sulfur atoms is 3.49(2) Å which is shorter than the sum of van der Waals radii of these atoms (3.65 Å),[3)] suggesting an electrostatic interaction between the chlorine and sulfur atoms <u>via</u> a charge transfer from the latter to the former. This is consistent with the result that the binding energies of Sn $3d_{3/2}$ and $3d_{5/2}$ electrons of the present salt (494.0 and 485.8 eV, respectively), determined from the X-ray photoelectron spectrum, are appreciably smaller than those of $Sn(CH_3)_2Cl_2$ (494.6 and 486.1 eV) and rather close to those of $[TTF]_3[Sn(CH_3)_2Cl_4]$ (494.0 and 485.5 eV),[1)] which involves a similar charge transfer interaction between the chlorine and sulfur atoms.

The trimerized tin(IV) anions are separated from each other along the $\underline{b}$ axis by disordered bonzonitrile molecules. On the other hand, planar DBTTF molecules constitute a columnar structure along the $\underline{b}$ axis with interplanar spacings of 3.47 (A/A'), 3.51 (A/B), 3.52 (B/C), and 3.45 Å (C/C'). Although the overlap modes of (A/A') and (C/C') are essentially the same as that of (A/B), that of (B/C) is somewhat insufficient (Fig. 2). Probably for this reason, the salt exhibits a rather large electrical resistivity (5.6 × 10^3 Ω cm) for a compacted pellet at 25 °C while the activation energy is small (0.057 eV).

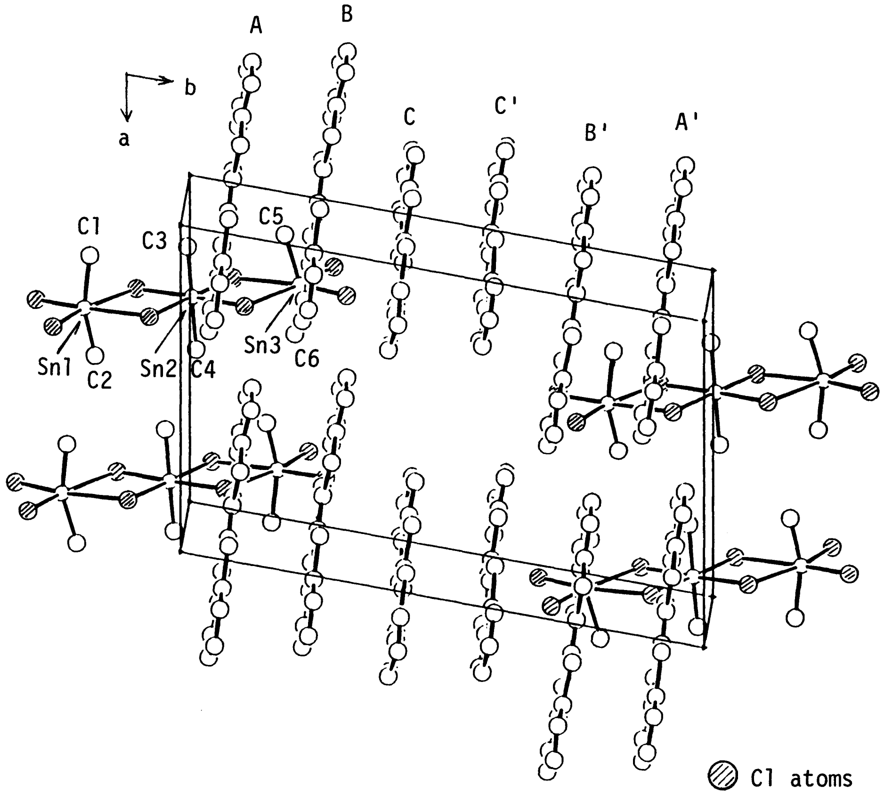
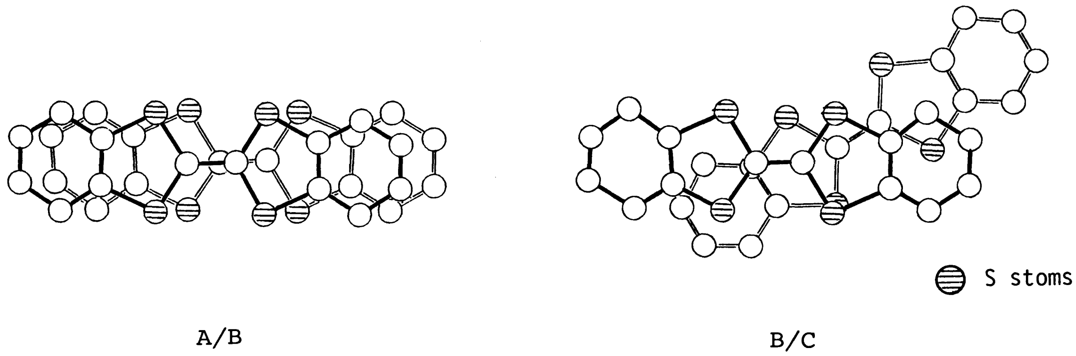


Fig. 1. Projection of the crystal structure of $[DBTTF]_3[Sn_3(CH_3)_6Cl_8]\cdot C_6H_5CN$ along the $\underline{c}^*$ axis. The disordered benzonitrile molecules are not illustrated for simplification.



A/B

B/C

Fig. 2. Overlaps of DBTTF molecules.

The molecules A and B seem to correspond to the $DBTTF^{+\cdot}$ radical cation and C to neutral DBTTF, since the central C-C distance of molecule C (1.35(5) Å) is somewhat shorter than those of A and B molecules (1.37(4) and 1.43(5) Å, respectively) and is close to that of neutral DBTTF (1.349(6) Å).[5] In accordance with this, the electronic reflectance spectrum of the present salt shows bands at 10800 and 8800 cm^{-1} which are tentatively assigned to $DBTTF^{+\cdot}/DBTTF^{+\cdot}$ and $DBTTF^{+\cdot}/DBTTF^{0}$ transitions, respectively, based on electronic spectra of tetrathiafulvalene[6] and dimethyldibenzotetrathiafulvalene salts.[7] Further studies on DBTTF salts with halogeno-organotin(IV) anions are now in progress.

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References

1) G. Matsubayashi, K. Ueyama, and T. Tanaka, J. Chem. Soc., Dalton Trans., 1985, 465.
2) K. Ueyama, G. Matsubayashi, R. Shimizu, and T. Tanaka, Polyhedron, submitted for publication.
3) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, New York (1960), p. 246.
4) Irrespective of the presence of apparently two different tin atoms in the anionic moiety, the spectrum has given only a respective peak for Sn $3d_{3/2}$ and $3d_{5/2}$ electrons.
5) R. P. Shibaeva, R. M. Lobkovskaya, and V. N. Klyuev, Cryst. Struct. Commun., 11, 835 (1982).
6) J. B. Torrance, B. A. Scott, B. Webster, F. B. Kaufman, and P. E. Seiden, Phys. Rev. B, 19, 730 (1979).
7) C. Tanaka, J. Tanaka, K. Dietz, C. Katayama, and M. Tanaka, Bull. Chem. Soc. Jpn., 56, 405 (1983).

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