# Synthesis and crystal structure of the deuterated organic conductor, $(d_8\text{-ET})_4[Hg_2(SCN)_4Cl_2]$

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On the basis of completely deuterated bis(ethylenedithio)tetrathiafulvalene ($d_8$-ET), new organic conductors, $(d_8\text{-ET})_4[Hg_2(SCN)_4Cl_2]$ and $(d_8\text{-ET})_2[Hg(SCN)_2Br]$ have been synthesized and studied by X-ray structural analysis. Unlike nondeuterated organic metals $k\text{-}(ET)_2[Hg(SCN)_{3-n}X_n]$ (X = Cl or Br; $n$ = 1 and 2), the crystal structure of $(d_8\text{-ET})_4[Hg_2(SCN)_4Cl_2]$ exhibits β-type packing of the $d_8$-ET radical cations in the conducting layer and a polymeric structure of anions, in which both the SCN groups and the Cl atoms are involved in the bridging bonds. The crystals of $(d_8\text{-ET})_2[Hg(SCN)_2Br]$ and the nondeuterated form $(ET)_2[Hg(SCN)_2Br]$ are isostructural.

**Key words:** deuterated bis(ethylenedithio)tetrathiafulvalene ($d_8$-ET), organic conductors, synthesis, crystal structure; X-ray structural analysis; intermolecular interactions.

The preparation and conducting properties of a new series of organic metals of the general formula $(ET)_2[Hg(SCN)_{3-n}X_n]$, where ET is bis(ethylenedithio)tetrathiafulvalene, X = F, Cl, Br, and I, and $n$ = 1 and 2 have previously been reported.[1] Chlorine- and bromine-containing salts of this series, $(ET)_2[Hg(SCN)_2Cl]$ (see Ref. 2), $(ET)_2[Hg(SCN)Cl_2]$, and $(ET)_2[Hg(SCN)_2Br]$ (see Ref. 3) have been studied by X-ray structural analysis. It has been demonstrated that these compounds belong to the same structural class and are characterized by æ-type packing of the ET cations in the conducting layers and by the polymeric structure of the anions formed owing to secondary interactions between the Hg atoms and the N atoms of the SCN groups. The Cl and Br atoms in these anions are terminal ligands not involved in the bonding of anions in the polymer chain.

Despite the structural similarity of the conductors studied, the temperatures of the metal—insulator transition ($T_{M-I}$) are substantially different. As the volume of the anion ($V$) decreases in the series $V_{[Hg(SCN)_2Br]} > V_{[Hg(SCN)_2Cl]} > V_{[Hg(SCN)Cl_2]}$, the $T_{M-I}$ temperature decreases (140, 50, and 35 K, respectively).[3] A similar correlation between $T_{M-I}$ and $V$ of anions has also been reported[4–6] for organic metals of the general formula $(ET)_8[Hg_4X_{12}(PhY)_2]$, where X, Y = Cl and Br.

It is known that even slight changes in the composition of cations of conducting salts affect their properties. Thus, the increase in the mass of radical cations in the salts of organic superconductors when H atoms are replaced with deuterium atoms leads to a change in the temperature of the transition to the superconducting state ($T_c$). Both the normal effect, when $T_c$ of the deuterated (D) form is lower than $T_c$ of the hydrogen (H) form (for example, in æ-$(ET)_2Cu[N(CN)_2]Br$), and the inverse effect, when $T_c$ of the D form is higher than that of the H form (in particular, in æ-$(ET)_2Cu(NCS)_2$ and æ-$(ET)_2Cu[N(CN)_2]Cl$) are observed (see Ref. 7).

Previously,[8] we have studied the structure of the completely deuterated organic superconductor $(d_8\text{-ET})_4[HgBr_2 \cdot Hg_2Br_6]$ and synthesized the completely deuterated salts $(d_8\text{-ET})_2[Hg(SCN)_2X]$, where X = Cl and Br. According to the results of preliminary X-ray structural analysis, the crystals of the D and H forms with X = Br are isostructural,[9] while in the case of the chlorine analog, substantial differences both in the crystal parameters and in the conducting properties were observed. The reasons for these differences became clear only when the structure of the D form was solved. Detailed results of X-ray structural analysis of the deuterated salt $(d_8\text{-ET})_4[Hg_2(SCN)_4Cl_2]$ (**1**) are given below.

## Experimental

Salt **1** was prepared by electrochemical oxidation of 9.8 mg of $d_8$-ET. A 9 : 1 mixture of trichloroethane and ethanol was used as the solvent, and a mixture of $Me_2NSCN$, KCl, and $Hg(SCN)_2$ was used as the electrolyte. Oxidation was performed in the potentiostatic mode ($I$ = 0.8 μA) at 40 °C.

The temperature dependence of the resistance of salt **1** has a metallic character, and its magnitude decreases by half when the temperature is decreased to 120 K. With a further decrease in temperature, the resistance increases sharply and salt **1** goes to the dielectric state ($T_{M-I}$ = 86 K, determined from the maximum of the logarithmic derivative).

Crystals of **1** were obtained as black thin plates with a typical metallic luster. The principal crystallographic data are as follows: $(C_{10}D_8S_8)_4[Hg_2(SCN)_4Cl_2]$, M = 2275.2, $a$ =

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19.348(5) Å, $b$ = 11.067(3) Å, $c$ = 9.717(3) Å, $\alpha$ = 114.28(3)°, $\beta$ = 106.90(2)°, $\gamma$ = 77.69(2)°, $V$ = 1806.2(7) Å$^3$, space group is $P\bar{1}$, $Z$ = 1, $d_{calc}$ = 2.11 g cm$^{-3}$, $F(000)$ = 1094, the crystal dimensions are 1.15×0.33×0.07 mm, $\mu$(Mo-K$\alpha$) = 5.4 cm$^{-1}$. Intensities of 3784 independent reflections with $I > 3\sigma(I)$ were measured on an automated four-circle KM-4 diffractometer (Kuma diffraction, Poland) ($\lambda$(Mo-K$\alpha$) = 0.7018 Å) equipped with a graphite monochromator using the $\theta/2\theta$ scanning technique in the range 2.0° < $\theta$ < 26.9°. The structure was solved by the direct method. The positions of D atoms were located from the difference synthesis; we failed to locate some D atoms. The structure was refined by the full-matrix least-squares method using anisotropic (for Hg, Cl, S, N, and C atoms) and isotropic (for D atoms) thermal parameters. An absorption correction was applied using the DIFABS program.[10] The weighting scheme was $w = 1/(a + F_{obs} + bF_{obs}^2)$, where $a = 2F_{min}$ and $b = 2/F_{max}$. The final value of the $R$ factor was 0.050. Atomic coordinates and equivalent isotropic temperature factors are given in Table 1. Interatomic distances and bond angles are given in Tables 2 and 3, respectively. All calculations were performed using the AREN-88 program package.[11]

## Results and Discussion

The crystal structure of salt **1** (Fig. 1) consists of alternating layers along the $a$ axis: anionic layers consisting of the $[Hg_2(SCN)_4Cl_2]^{2-}$ dimers and cationic

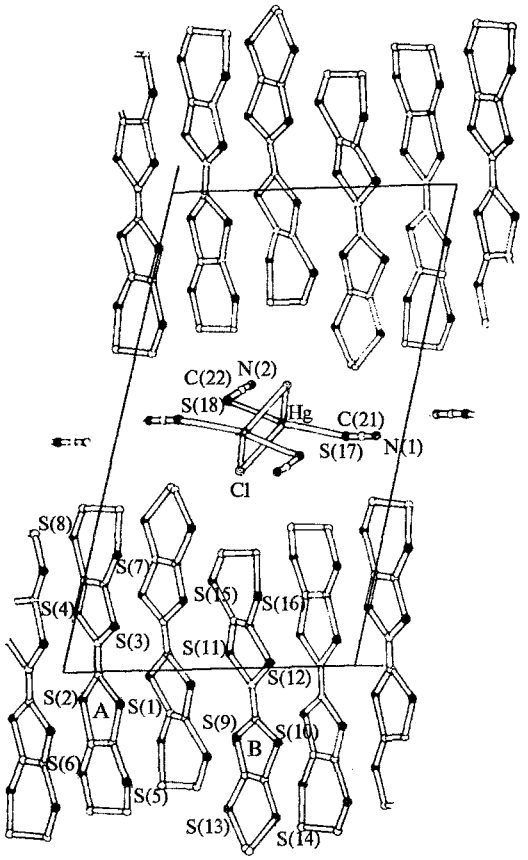



**Fig. 1.** Projection of the crystal structure of $(d_8\text{-ET})_4[Hg_2(SCN)_4Cl_2]$ onto the $ab$ plane.

**Table 1.** Atomic coordinates (×10$^4$ for Hg, Cl, S, N, and C atoms and ×10$^3$ for D atoms) and equivalent isotropic temperature factors ($B_{iso}$) in the structure of $(d_8\text{-ET})_4[Hg_2(SCN)_4Cl_2]$

| Atom | $x$ | $y$ | $z$ | $B_{iso}$/Å$^2$ |
|---|---|---|---|---|
| Hg | 5084(1) | 5591(1) | 3409(1) | 7.87 |
| Cl | 4096(1) | 4552(3) | 3850(3) | 7.72 |
| S(1) | 9294(1) | 2195(3) | −171(3) | 7.22 |
| S(2) | 9473(1) | 775(3) | −3378(3) | 7.01 |
| S(3) | 10955(1) | 1394(3) | 1166(3) | 7.13 |
| S(4) | 11196(1) | −30(3) | −1997(3) | 7.06 |
| S(5) | 7736(1) | 3063(3) | −1020(3) | 7.34 |
| S(6) | 7954(1) | 1381(3) | −4861(3) | 7.41 |
| S(7) | 12465(1) | 912(3) | 2768(3) | 7.55 |
| S(8) | 12771(1) | −737(3) | −1009(3) | 7.68 |
| S(9) | 8618(1) | 6411(3) | 1026(3) | 7.12 |
| S(10) | 8444(1) | 7889(3) | 4220(3) | 7.04 |
| S(11) | 10332(1) | 5566(3) | 2388(3) | 7.42 |
| S(12) | 10101(1) | 6983(3) | 5560(3) | 7.37 |
| S(13) | 7064(1) | 6673(3) | −468(3) | 7.42 |
| S(14) | 6842(1) | 8451(3) | 3352(3) | 8.56 |
| S(15) | 11829(1) | 4451(3) | 3323(3) | 8.10 |
| S(16) | 11558(1) | 6082(3) | 7078(3) | 8.61 |
| S(17) | 4824(2) | 7978(4) | 4005(5) | 9.94 |
| S(18) | 5658(2) | 3487(3) | 1803(4) | 8.36 |
| N(1) | 4807(12) | 9010(19) | 7168(24) | 14.95 |
| N(2) | 5915(8) | 4207(14) | −440(15) | 10.03 |
| C(1) | 9866(6) | 1230(11) | −1411(12) | 6.76 |
| C(2) | 10588(6) | 906(11) | −798(12) | 6.71 |
| C(3) | 8520(5) | 2193(10) | −1667(13) | 6.53 |
| C(4) | 8605(5) | 1558(10) | −3131(12) | 6.46 |
| C(5) | 11839(5) | 683(11) | 979(13) | 6.70 |
| C(6) | 11960(5) | 51(11) | −438(12) | 6.64 |
| C(7) | 7145(7) | 3195(19) | −2751(17) | 10.05 |
| C(8) | 7116(7) | 1981(17) | −4183(17) | 9.80 |
| C(9) | 13310(7) | 642(15) | 2204(17) | 8.57 |
| C(10) | 13391(6) | −645(13) | 865(14) | 7.96 |
| C(11) | 9013(6) | 6898(11) | 3006(11) | 6.57 |
| C(12) | 9726(6) | 6531(10) | 3580(12) | 6.60 |
| C(13) | 7734(6) | 7049(10) | 1265(12) | 6.68 |
| C(14) | 7652(5) | 7698(11) | 2722(13) | 6.85 |
| C(15) | 11053(6) | 5423(11) | 3914(13) | 6.78 |
| C(16) | 10946(6) | 6048(11) | 5356(13) | 6.95 |
| C(17) | 6272(7) | 7680(17) | 201(16) | 9.14 |
| C(18) | 6168(8) | 7718(19) | 1636(17) | 10.24 |
| C(19) | 12462(7) | 4555(19) | 5100(17) | 9.79 |
| C(20) | 12412(7) | 5753(15) | 6500(20) | 10.25 |
| C(21) | 4834(8) | 8547(16) | 5860(22) | 9.35 |
| C(22) | 5800(6) | 3958(11) | 477(14) | 7.30 |
| D(71) | 664(6) | 360(11) | −256(13) | |
| D(72) | 689(9) | 230(16) | −280(19) | |
| D(81) | 670(5) | 221(9) | −515(11) | |
| D(82) | 734(7) | 280(12) | −420(15) | |
| D(91) | 1373(6) | 63(11) | 341(13) | |
| D(101) | 1382(7) | −82(14) | 66(16) | |
| D(102) | 1327(6) | −144(11) | 109(12) | |
| D(171) | 598(5) | 744(9) | −55(11) | |
| D(172) | 640(8) | 866(15) | 24(17) | |
| D(181) | 572(11) | 824(21) | 174(24) | |
| D(191) | 1280(8) | 468(15) | 528(17) | |
| D(201) | 1275(7) | 555(14) | 747(16) | |
| D(202) | 1224(8) | 487(14) | 641(17) | |

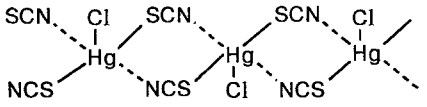
layers formed by two crystallographically independent $d_8$-ET radical cations denoted by A and B. Unlike the

**Table 2.** Bond lengths (*d*) in molecule **1**

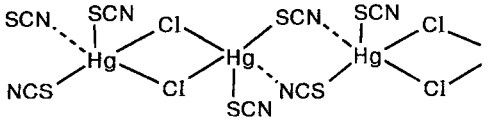
| Bond | *d*/Å | Bond | *d*/Å |
|---|---|---|---|
| Hg—Cl | 2.640(4) | Hg—Cl | 2.723(3) |
| Hg—S(17) | 2.432(4) | Hg—S(18) | 2.452(3) |
| S(1)—C(1) | 1.74(1) | S(1)—C(3) | 1.76(1) |
| S(2)—C(1) | 1.74(1) | S(2)—C(4) | 1.75(1) |
| S(3)—C(2) | 1.72(1) | S(3)—C(5) | 1.75(1) |
| S(4)—C(2) | 1.76(1) | S(4)—C(6) | 1.77(1) |
| S(5)—C(3) | 1.75(1) | S(5)—C(7) | 1.78(2) |
| S(6)—C(4) | 1.75(1) | S(6)—C(8) | 1.82(2) |
| S(7)—C(5) | 1.76(1) | S(7)—C(9) | 1.80(2) |
| S(8)—C(6) | 1.75(2) | S(8)—C(10) | 1.84(1) |
| S(9)—C(11) | 1.75(1) | S(9)—C(13) | 1.75(1) |
| S(10)—C(11) | 1.73(1) | S(10)—C(14) | 1.76(1) |
| S(11)—C(12) | 1.76(1) | S(11)—C(15) | 1.75(1) |
| S(12)—C(12) | 1.74(1) | S(12)—C(16) | 1.76(1) |
| S(13)—C(13) | 1.75(1) | S(13)—C(17) | 1.81(1) |
| S(14)—C(14) | 1.76(1) | S(14)—C(18) | 1.79(1) |
| S(15)—C(15) | 1.75(1) | S(15)—C(19) | 1.78(1) |
| S(16)—C(16) | 1.74(1) | S(16)—C(20) | 1.81(2) |
| S(17)—C(21) | 1.64(2) | S(18)—C(22) | 1.68(2) |
| N(1)—C(21) | 1.17(3) | N(2)—C(22) | 1.12(2) |
| C(1)—C(2) | 1.38(1) | C(3)—C(4) | 1.34(2) |
| C(5)—C(6) | 1.33(2) | C(7)—C(8) | 1.48(2) |
| C(9)—C(10) | 1.50(2) | C(11)—C(12) | 1.37(1) |
| C(13)—C(14) | 1.34(2) | C(15)—C(16) | 1.34(2) |
| C(17)—C(18) | 1.45(3) | C(19)—C(20) | 1.47(2) |

structure of the H form, in which the anionic layers contain single-charged monomeric $[Hg(SCN)_2Cl]^-$ anions, in the structure of **1** (the D form), the anionic layers consist of doubly charged $\left[(SCN)_2Hg\langle^{Cl}_{Cl}\rangle Hg(SCN)_2\right]^{2-}$ dimers. However, in both structures, the anions form polymer chains (Schemes 1 and 2, respectively) owing to shortened intermolecular Hg...NCS contacts (2.75(3) and 2.98(8) Å in the H form and 3.04(1) Å in the D form; the sum of van der Waals radii of Hg and N is 3.25 Å).

**Scheme 1**




**Scheme 2**




The Hg...Hg distances in the D form, **1**, are 3.932(1) and 6.125(1) Å. Therefore, both the SCN groups and the Cl atoms are involved in the formation of the polymeric structure of the anion of the D form. However, in all the structures of the $(ET)_2[Hg(SCN)_{3-n}X_n]$ conductors studied previously,[2,3] the formation of polymer anionic chains occurs only through SCN bridging groups.

A comparison of the anionic chains in the D form, **1**, and in the H form, $(ET)_2[Hg(SCN)_2Cl]$, demonstrates that the isotopic substitution leads to a change in the coordinating function of the SCN and Cl ligands. Thus, in the structure of the H form, $(ET)_2[Hg(SCN)_2Cl]$, the Cl atom is terminal, while both SCN groups are bridging. In the structure of the D form, **1**, both Cl atoms and one SCN group are bridging, while the other SCN group is terminal. As a result of this coordination rearrangement of the ligands in the structure of **1**, the $[(SCN)_2Hg_2Cl_2(SCN)_2]^{2-}$ anions are dimerized, and Cl atoms as well as SCN groups participate in the forma-

**Table 3.** Bond angles (ω) in molecule **1**

| Angle | ω/deg | Angle | ω/deg |
|---|---|---|---|
| Cl—Hg—S(17) | 113.8(2) | Cl—Hg—S(18) | 96.8(2) |
| Cl—Hg—Cl′ | 85.7(2) | S(17)—Hg—S(18) | 145.4(2) |
| S(17)—Hg—Cl′ | 103.0(2) | S(18)—Hg—Cl′ | 94.7(1) |
| Hg—Cl—Hg′ | 94.3(2) | Cl—Hg—N(2′) | 145.4(2) |
| C(1)—S(1)—C(3) | 94.9(7) | C(1)—S(2)—C(4) | 95.1(7) |
| C(2)—S(3)—C(5) | 95.0(7) | C(2)—S(4)—C(6) | 95.5(7) |
| C(3)—S(5)—C(7) | 102(1) | C(4)—S(6)—C(8) | 101.9(8) |
| C(5)—S(7)—C(9) | 101.9(8) | C(6)—S(8)—C(10) | 101.3(8) |
| C(11)—S(9)—C(13) | 95.0(7) | C(11)—S(10)—C(14) | 94.7(7) |
| C(12)—S(11)—C(15) | 95.0(7) | C(12)—S(12)—C(16) | 95.4(7) |
| C(13)—S(13)—C(17) | 101.6(7) | C(14)—S(14)—C(18) | 102(1) |
| C(15)—S(15)—C(19) | 103(1) | C(16)—S(16)—C(20) | 100.5(8) |
| S(1)—C(1)—S(2) | 116(1) | S(1)—C(1)—C(2) | 119.6(4) |
| S(2)—C(1)—C(2) | 125(1) | S(3)—C(2)—S(4) | 116(1) |
| S(3)—C(2)—C(1) | 123(1) | S(4)—C(2)—C(1) | 121.5(4) |
| S(1)—C(3)—S(5) | 114.2(3) | S(1)—C(3)—C(4) | 117(1) |
| S(5)—C(3)—C(4) | 129(1) | S(2)—C(4)—S(6) | 114.3(5) |
| S(2)—C(4)—C(3) | 117(3) | S(6)—C(4)—C(3) | 128(1) |
| S(3)—C(5)—S(7) | 113.5(6) | S(3)—C(5)—C(6) | 118(1) |
| S(7)—C(5)—C(6) | 128(2) | S(4)—C(6)—S(8) | 114.2(4) |
| S(4)—C(6)—C(5) | 116(1) | S(8)—C(6)—C(5) | 129(1) |
| S(5)—C(7)—C(8) | 117(1) | S(6)—C(8)—C(7) | 116(2) |
| S(7)—C(9)—C(10) | 113(2) | S(8)—C(10)—C(9) | 116(1) |
| C(11)—S(9)—C(13) | 95.0(7) | C(11)—S(10)—C(14) | 94.7(7) |
| C(12)—C(11)—C(15) | 95.0(7) | C(12)—S(12)—C(16) | 95.4(7) |
| C(13)—S(13)—C(17) | 101.6(7) | C(14)—S(14)—C(18) | 102(1) |
| C(15)—S(15)—C(19) | 103(1) | C(16)—S(16)—C(20) | 100.5(8) |
| Hg—S(17)—C(21) | 101.4(9) | Hg—S(18)—C(22) | 100.2(5) |
| S(9)—C(11)—S(10) | 115(1) | S(9)—C(11)—C(12) | 123(1) |
| S(10)—C(11)—C(12) | 121.5(1) | S(11)—C(12)—S(14) | 115(1) |
| S(11)—C(12)—C(11) | 123.0(4) | S(12)—C(12)—C(11) | 122(1) |
| S(9)—C(13)—S(13) | 114.4(5) | S(9)—C(13)—C(14) | 117(1) |
| S(13)—C(13)—C(14) | 129(2) | S(10)—C(14)—S(14) | 14.7(3) |
| S(10)—C(14)—C(13) | 117(2) | S(14)—C(14)—C(13) | 128(1) |
| S(11)—C(15)—S(15) | 114.1(4) | S(11)—C(15)—C(16) | 117(1) |
| S(15)—C(15)—C(16) | 128(1) | S(12)—C(16)—C(14) | 115.3(6) |
| S(12)—C(16)—C(15) | 117(1) | S(16)—C(16)—C(15) | 128(2) |
| S(13)—C(17)—C(18) | 117(2) | S(14)—C(18)—C(17) | 116(2) |
| S(15)—C(19)—C(20) | 119(2) | S(16)—C(20)—C(19) | 114(2) |
| S(17)—C(21)—N(1) | 176(2) | S(18)—C(22)—N(2) | 176(1) |

tion of polymer chains. Because the same $Hg(SCN)_2Cl$ group is the basic unit of both polymer chains, the anionic chains in the H and D forms can be considered as isomers.

The $[Hg_2(SCN)_4Cl_2]^{2-}$ anion has a centrosymmetric dimeric structure (see Fig. 1). Each Hg atom is surrounded by two Cl atoms and two SCN groups and is characterized by the tetrahedral configuration of the Hg—Cl and Hg—S bonds. The Hg—Cl bonds [2.640(4) and 2.723(3) Å] in the planar four-membered cycle are substantially elongated compared to the distances between the Hg atoms and the terminal Cl atoms in the structures studied previously: $(ET)_2[Hg(SCN)_2Cl]$ [2.383(7) Å],[2] $(ET)_2[Hg(SCN)Cl_2]$ [2.354(3) and 2.478(7) Å],[3] $(EPT)HgCl_3$ [2.343(3)—2.449(3) Å],[12] and $(ET)_8[Hg_4Cl_{12}(PhCl)_2]$ [2.372(4)—2.542(4) Å].[5] The elongation of the Hg—Cl bonds observed in the dimer is due to the participation of Cl atoms in the formation of bridges. This fact is strongly supported by the Hg—Cl bond lengths in the dimer structures containing both terminal and bridging Cl atoms. In all these structures, the $Hg—Cl_{br}$ bridging bonds are longer than the $Hg—Cl_{term}$ terminal bonds; the difference in their lengths changes rather significantly and is determined by particular structural conditions: 2.584(4) and 2.360(4) Å in $[Hg(dapmp)Cl]_{0.5}[Hg_2Cl_6]$,[13] 2.793(6) and 2.391(6) Å in $(ET)_3[HgCl_3]_2$,[14] 2.759(3) and 2.350(3) Å in the $Hg_2Cl_6^{2-}$ anion, and 2.880(3) and 2.344(3) Å in the $[Hg_4Cl_{14}]^{6-}$ anion of the $[Cr(dien)_2][Hg_2Cl_7]$ structure.[15]

The elongation of the bonds with terminal Cl atoms demonstrated above and with atoms of other halogens in the $(ET)_4[Hg_2Br_6](TCE)$ [16] and $(ET)_4Cd_2I_6$ [17] salts, which is understandable in terms of chemical bond theory, is not supported so strongly in the case of SCN ligands. Thus, of the two SCN groups bonded to Hg atoms in the structure of **1**, one group, S(17)C(21)N(1), is terminal, while the other, S(18)C(22)N(2), is bridging. Despite this difference, the $Hg—S(18)_{br}$ and $Hg—S(17)_{term}$ bond lengths [2.452(3) and 2.432(4) Å, respectively] are essentially identical. Probably, the structure of **1** is unusual and cannot be considered in the elucidation of the true relationship between the bond lengths of the Hg atom with bridging and terminal SCN ligands. Thus, in the series of structures studied previously: $(ET)_2[Hg(SCN)_2Cl]$,[2] $(ET)_2[Hg(SCN)Cl_2]$,[3] and $(ET)_2[Hg(SCN)_2Br]$,[3] in which all SCN groups are bridging ligands, the $Hg—(SCN)_{br}$ bonds are slightly longer [2.490(1)—2.513(7) Å]. The Hg—SCN bond lengths in the salts with tetrahedral anions, $(ET)_2[HgK(SCN)_4]$ [18] and $(ET)_2[HgNH_4(SCN)_4]$ [18] are even larger [2.545(2)—2.569(4) Å]. Therefore, the distances of 2.432(3) and 2.452(3) Å between the Hg atoms and the SCN groups in the structure of **1** correspond to the lower limit of the range of the Hg—SCN bond lengths reported in the literature. This makes it possible to conclude that the interaction between Hg and SCN in the structure of **1** is mainly covalent in nature. The bond lengths and bond angles in the thiocyanate groups correspond to the mean-statistical values.[19]

The characteristic feature of the crystal structures of conducting organic salts with mercury-containing anions is the participation of Hg atoms in secondary interactions of the Hg...X type, where X = Cl, Br, and NCS. In the structure of **1**, this interaction occurs between the Hg atom and the N(2) atom of the bridging N(2)C(22)S(18) group. Taking into account this interaction, the Hg...N(2) ($1-x$, $1-y$, $-z$) distance is 3.04(1) Å, the coordination surroundings of Hg increases to five atoms, and the tetrahedral configuration of the bonds changes to trigonal-bipyramidal (see Table 2). The equatorial plane of this bipyramid is formed by the Cl, S(17), and S(18) atoms, and the Cl′ and N(2′) atoms occupy apical positions. The Hg atom deviates from the equatorial plane by 0.42 Å toward the Cl′ atom.

In the radical cation A, the maximum deviation of atoms from the mean plane (excluding the ethylene groups) is no more than 0.08 Å (see Table 2). The

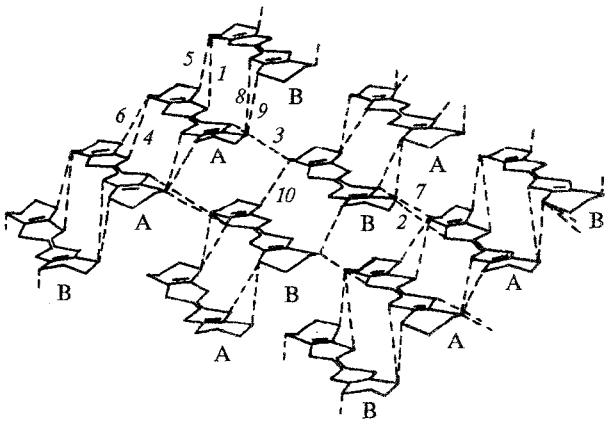



**Fig. 2.** Packing of $d_8$-ET radical cations in the conducting layer of the $(d_8\text{-ET})_4[Hg_2(SCN)_4Cl_2]$ structure. The types of contacts are denoted by numbers (see Table 4).

**Table 4.** Shortened S...S intercation contacts (<3.68 Å) in the structure of **1**

| Contact | *d*(S...S)/Å | Symmetry operation | Contact type* |
|---|---|---|---|
| S(1)...S(16) | 3.495(4) | $1-x$, $1-y$, $1-z$ | *1* |
| S(2)...S(10) | 3.672(4) | $x$, $y-1$, $z-1$ | *2* |
| S(3)...S(15) | 3.640(4) | $x$, $y$, $z$ | *3* |
| S(4)...S(6) | 3.518(4) | $1-x$, $-y$, $-(z+1)$ | *4* |
| S(5)...S(16) | 3.459(4) | $1-x$, $1-y$, $1-z$ | *5* |
| S(6)...S(8) | 3.659(4) | $1-x$, $-y$, $-(z+1)$ | *6* |
| S(6)...S(10) | 3.568(4) | $x$, $y-1$, $z-1$ | *7* |
| S(7)...S(10) | 3.497(4) | $1-x$, $1-y$, $1-z$ | *8* |
| S(7)...S(14) | 3.433(4) | $1-x$, $1-y$, $1-z$ | *9* |
| S(13)..S(15) | 3.648(4) | $1-x$, $2-y$, $1-z$ | *10* |

* For the designations of contacts, see Fig. 2.

ethylene groups are in an eclipsed conformation: the C(7) and C(9) atoms are located −0.40 and −0.53 Å, respectively, below the mean plane, while the C(8) and C(10) atoms are located 0.27 and 0.18 Å above this plane. The characteristic feature of the conformation of radical cation B is the nonplanar structure of the TTF fragment: the five-membered rings are tilted with respect to each other by 11.0(5)°. As a result, the S and C($sp^2$) atoms deviate substantially (from −0.10 to 0.30 Å) from the mean plane of the radical cation. The ethylene groups, like in cation A, are in the eclipsed conformation. The deviations of the C(17), C(18), C(19), and C(20) atoms from the mean plane of the cation are 0.23, −0.37, −0.30, and 0.32 Å, respectively.

The cationic layers consist of radical cations A and B. Unlike the *k*-type structure of the conducting layer in the nondeuterated salt $(ET)_2[Hg(SCN)_2Cl]$,[2] in the crystal of **1**, $d_8$-ET radical cations are packed into a β-type structure (Fig. 2). The shortened S...S intercation contacts are shown in Fig. 2, and their lengths are given in Table 4.

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