Synthesis and crystal structure of the deuterated organic conductor, 
\((d_8-\text{ET})_4[\text{Hg}_2(\text{SCN})_4\text{Cl}_2]\)

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On the basis of completely deuterated bis(ethylenedithio)tetrathiafulvalene (d-ET), new organic conductors, \((d_8-\text{ET})_4[\text{Hg}_2(\text{SCN})_4\text{Cl}_2]\) and \((d_8-\text{ET})_2[\text{Hg}(\text{SCN})_2\text{Br}]\) have been synthesized and studied by X-ray structural analysis. Unlike nondeuterated organic metals \(k-(\text{ET})_2[\text{Hg}(\text{SCN})_3\text{X}_n]\) (\(X = \text{Cl} \) or Br; \(n = 1 \) and 2), the crystal structure of \((d_8-\text{ET})_4[\text{Hg}_2(\text{SCN})_4\text{Cl}_2]\) exhibits \(\beta\)-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 \((d_8-\text{ET})_2[\text{Hg}(\text{SCN})_2\text{Br}]\) and the nondeuterated form \((\text{ET})_2[\text{Hg}(\text{SCN})_2\text{Br}]\) are isostructural.

**Key words:** deuterated bis(ethylenedithio)tetrathiafulvalene (d-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 \(\text{(ET)}_2[\text{Hg}(\text{SCN})_3-n\text{X}_n]\), where ET is bis(ethylenedithio)tetrathiafulvalene, \(X = \text{F}, \text{Cl}, \text{Br}, \) and \(I\), and \(n = 1 \) and 2 have previously been reported.\(^1\) Chlorine- and bromine-containing salts of this series, \(\text{(ET)}_2[\text{Hg}(\text{SCN})_2\text{Cl}]\) (see Ref. 2), \(\text{(ET)}_2[\text{Hg}(\text{SCN})_2\text{Cl}_2]\), and \(\text{(ET)}_2[\text{Hg}(\text{SCN})_2\text{Br}]\) (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 \(\pi\)-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 \(T_{\text{M-I}}\) are substantially different. As the volume of the anion \(V\) decreases in the series \(V_{\text{[Hg(SCN)_2Br]}} > V_{\text{[Hg(SCN)_2Cl]}} > V_{\text{[Hg(SCN)_2Cl}_2]}\), the \(T_{\text{M-I}}\) temperature decreases \((140, 50, \) and 35 K, respectively).\(^3\) A similar correlation between \(T_{\text{M-I}}\) and \(V\) of anions has also been reported\(^4-6\) for organic metals of the general formula \(\text{(ET)}_8[\text{H}_8\text{X}_2(\text{Ph})_2]\), where \(X = \text{Cl} \) 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 D form is lower than that of the H form (in particular, in \(\varepsilon-(\text{ET})_2\text{Cu}[\text{N(CN)}_2]\), and the inverse effect, when \(T_c\) of the D form is higher than that of the H form (for example, in \(\varepsilon-(\text{ET})_2\text{Cu}[\text{N(CN)}_2]\)) are observed (see Ref. 7).

Previously,\(^8\) we have studied the structure of the completely deuterated organic superconductor \((d_8-\text{ET})_4[\text{HgBr}_2\cdot\text{Hg}_2\text{Br}_6]\) and synthesized the completely deuterated salts \((d_8-\text{ET})_2[\text{Hg}(\text{SCN})_2\text{X}]\), where \(X = \text{Cl} \) and Br. According to the results of preliminary X-ray structural analysis, the crystals of the D and H forms with \(X = \text{Br}\) 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 \((d_8-\text{ET})_4[\text{Hg}_2(\text{SCN})_4\text{Cl}_2]\) (I) are given below.

**Experimental**

Salt I 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, KC_1, and Hg(SCN)_2 was used as the electrolyte. Oxidation was performed in the potentiostatic mode \((I = 0.8 \mu\text{A})\) at 40 °C.

The temperature dependence of the resistance of salt I 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 I goes to the dielectric state \((T_{\text{M-I}} = 86 \text{ K})\) determined from the maximum of the logarithmic derivative.

Crystals of I were obtained as black thin plates with a typical metallic luster. The principal crystallographic data are as follows: \((\text{C}_{10}\text{D}_{8}\text{S}_8)_4[\text{Hg}_2(\text{SCN})_4\text{Cl}_2]\), \(M = 2275.2, a = \)
Synthesis and structure of \((\text{ds-ET})_4[Hg_2(\text{SCN})_4\text{Cl}_2]\) 


19.348(5) Å, \(b = 11.067(3)\) Å, \(c = 9.717(3)\) Å, \(\alpha = 114.28(3)^\circ\), \(\beta = 106.90(2)^\circ\), \(\gamma = 77.69(2)^\circ\), \(V = 1806.2(7)\) Å³, space group is \(P1\), \(Z = 1\), \(\rho_{\text{calc}} = 2.11\ \text{g cm}^{-3}\), \(F(000) = 1094\), the crystal dimensions are \(1.15 \times 0.33 \times 0.07\) mm, \(\mu(\text{Mo-K}α) = 5.4\ \text{cm}^{-1}\). Intensities of 3784 independent reflections with \(I > 3\sigma(I)\) were measured on an automated four-circle KM-4 diffractometer (Kuma diffraction, Poland) \((\lambda(\text{Mo-K}α) = 0.7018\ \text{Å})\) equipped with a graphite monochromator using the 0/2θ scanning technique in the range 2.0° < 2θ < 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 \(w = 1/(a + F_{\text{obs}} + bF_{\text{obs}}^2)\), where \(a = 2F_{\text{min}}\) and \(b = 2/F_{\text{max}}\). 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 I (Fig. 1) consists of alternating layers along the \(a\) axis: anionic layers consisting of the \([Hg_2(\text{SCN})_4\text{Cl}_2]^{2-}\) dimers and cationic layers formed by two crystallographically independent \(\text{ds-ET}\) radical cations denoted by A and B. Unlike the

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Table 1. Atomic coordinates (\(\times 10^4\) for Hg, Cl, S, N, and C atoms and \(\times 10^3\) for D atoms) and equivalent isotropic temperature factors (\(B_{\text{iso}}\)) in the structure of \((\text{ds-ET})_4[Hg_2(\text{SCN})_4\text{Cl}_2]\)

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Fig. 1. Projection of the crystal structure of \((\text{ds-ET})_4[Hg_2(\text{SCN})_4\text{Cl}_2]\) onto the \(ab\) plane.