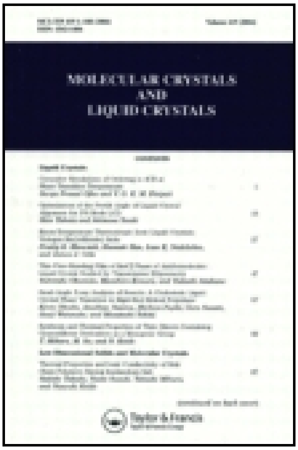

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Structure of Bis(ethylenedithio)tetrathiafulvalenium Dichlorocyanoselenate (2:1), (BEDT-TTF)$_2$Cl$_2$SeCN

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STRUCTURE OF BIS(ETHYLENEDITHIO)TETRATHIAFULVALENIUM DICHLOROCYANOSELENATE (2:1), $(BEDT\text{-}TTF)_2Cl_2SeCN$

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Abstract The synthesis and crystal structure of the new organic semiconductor $(BEDT\text{-}TTF)_2Cl_2SeCN$ [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] is described. The salt is isostructural with $(BEDT\text{-}TTF)_2Br_2SeCN$, reported earlier.

INTRODUCTION

The electron donor molecule BEDT-TTF has yielded approximately 50 superconductors to date (for a review, see ref. 1). In addition, numerous other salts with a variety of electrical and magnetic properties have been discovered. Recently, we reported a semiconducting salt of BEDT-TTF with the novel *T*-shaped anion Br_2SeCN^-.[2] The crystallographic analysis of that salt revealed a near-centrosymmetric triclinic structure, except for the symmetry-breaking anion. On the basis of a Hamilton *R*-value test, the non-centrosymmetric space group $P1$ with ordered anions was preferred over centrosymmetric $P\bar{1}$ with disordered anions. In this paper, we present the synthesis and crystal structure of the isostructural chlorine-analogue salt $(BEDT\text{-}TTF)_2Cl_2SeCN$.

SYNTHESIS AND PHYSICAL PROPERTIES

The title compound was formed by the standard electrocrystallization method.[3] The BEDT-TTF donor molecule was electrolytically oxidized in an 1,1,2-trichloroethane solution containing the previously isolated, dark red solid precipitated with petroleum ether from a dichloromethane solution of $KAuCl_4$, KSeCN, and (cat)Cl (cat = tetraphenylarsonium). The anion species should have been $(cat)Au(SeCN)_4$,[4] but it was found to be deficient in $SeCN^-$ and also contained chlorine, based on elemental analysis. Under application of a current density of 4.5×10^{-3} A m^{-2}, lustrous black, rod-like crystals appeared after six days and grew for a further ten days before they were harvested. No attempts were made to crystallize the title compound directly from a Cl_2SeCN^- salt.[5] The crystals were tested for superconductivity, with negative results, at ambient pressure and at temperatures as low as 4.2 K, on an ac susceptometer (Lake

Shore Cryotronics, Inc.). The electrical conductivity (four-probe method) was activated between 100 and 300 K, with a room temperature resistivity of ca. 0.04 Ωm. A broad phase transition was indicated by an increase of the resistivity between 175 and 165 K by a factor of twenty. The activation energies were 0.17 and 0.08 eV above and below the phase transition, respectively.

CRYSTAL STRUCTURE

Single crystal X-ray diffraction experiments were carried out at room temperature on a modifed Nicolet *P*3 four-circle diffractometer equipped with a Mo sealed tube and a graphite monochromator ($\lambda = 0.7107$ Å). ω-scan intensity data to $2\theta_{max} = 56°$ were corrected for Lorentz, polarization, and absorption effects. Of the 3979 unique reflections, 2748 with $I > 2\sigma$ were employed in the analysis. Starting atomic coordinates were obtained from the analogous Br_2SeCN^- salt.[2]

TABLE I Lattice parameters of $(BEDT\text{-}TTF)_2X_2SeCN$ (X = Cl, Br[2]) at room temperature ($Z = 1$).

	X = Cl	X = Br
a (Å)	5.9239(7)	5.9304(6)
b (Å)	8.7216(11)	8.8042(9)
c (Å)	16.249(2)	16.509(2)
α(°)	95.030(4)	95.723(8)
β(°)	98.981(4)	98.767(8)
γ(°)	92.688(4)	92.192(8)
V (Å^3)	824.5(2)	846.4(2)

The lattice constants of the title compound (Table I) were very similar to those of the isostructural Br_2SeCN^- salt. The largest differences were 0.26(2) Å and 0.69(4)° for *c*-axis and the α-angle, respectively. A detailed description of the layered crystal structure of $(BEDT\text{-}TTF)_2Br_2SeCN$ has been published,[2] and the overall features of the present salt are the same (see Tables II and III for atomic coordinates and geometrical results, respectively). The packing of the BEDT-TTF donor molecules in the conducting layer is shown in Figure 1.

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters in (BEDT-TTF)$_2$Cl$_2$SeCN.

Atom	x	y	z	U_{eq} (Å^2)
Se	0.0	0.0	0.0	0.0552(3)
Cl1	0.0125(13)	0.2612(8)	−0.0386(4)	0.058(2)
Cl2	0.0112(13)	−0.2641(8)	0.0394(4)	0.057(2)
N	0.509(5)	0.000(4)	0.008(2)	0.085(5)
C0	0.292(2)	0.0041(14)	−0.0011(6)	0.053(4)
S1	0.2653(12)	0.1471(10)	0.5184(4)	0.051(2)
S2	0.7105(12)	0.2995(8)	0.5907(3)	0.044(2)
S3	0.3217(11)	0.2564(8)	0.3397(4)	0.051(2)
S4	0.7685(12)	0.4061(8)	0.4080(4)	0.044(2)
S5	0.1679(12)	0.0223(8)	0.6695(4)	0.057(2)
S6	0.6913(12)	0.2124(10)	0.7599(4)	0.068(3)
S7	0.3290(11)	0.3150(9)	0.1659(4)	0.056(2)
S8	0.8728(11)	0.4862(8)	0.2445(4)	0.056(2)
C1	0.495(3)	0.254(2)	0.5017(10)	0.034(5)
C2	0.522(3)	0.297(2)	0.4225(9)	0.030(5)
C3	0.358(3)	0.126(2)	0.6194(11)	0.035(6)
C4	0.555(3)	0.197(2)	0.6579(11)	0.047(6)
C5	0.477(4)	0.334(2)	0.2704(11)	0.046(7)
C6	0.683(2)	0.405(2)	0.2999(8)	0.022(4)
C7	0.292(4)	0.066(3)	0.7771(12)	0.083(9)
C8	0.532(2)	0.088(2)	0.8088(11)	0.072(6)
C9*A*	0.600(6)	0.327(3)	0.118(2)	0.042(5)^{i}
C9*B*	0.503(5)	0.420(3)	0.112(2)	$= U_{iso}$(C9*A*)
C10*A*	0.780(6)	0.452(4)	0.136(2)	0.034(5)^{i}
C10*B*	0.775(4)	0.386(3)	0.139(2)	$= U_{iso}$(C10*A*)
S11	0.7494(12)	0.8520(10)	0.4836(4)	0.048(2)
S12	0.3050(12)	0.7004(9)	0.4094(4)	0.051(2)
S13	0.6967(11)	0.7404(9)	0.6609(4)	0.048(2)
S14	0.2421(11)	0.5952(8)	0.5932(4)	0.043(2)
S15	0.8410(12)	0.9747(9)	0.3289(4)	0.062(2)
S16	0.3132(13)	0.7901(11)	0.2393(4)	0.068(3)
S17	0.6773(11)	0.6871(8)	0.8353(4)	0.051(2)
S18	0.1350(11)	0.5105(8)	0.7538(4)	0.051(2)
C11	0.493(3)	0.746(2)	0.4972(11)	0.038(5)
C12	0.478(3)	0.696(2)	0.5702(11)	0.040(6)

Table II continued.

C13	0.651(3)	0.868(2)	0.3750(9)	0.044(6)
C14	0.445(3)	0.796(2)	0.3447(11)	0.036(6)
C15	0.546(2)	0.657(2)	0.7316(10)	0.032(5)
C16	0.343(4)	0.592(2)	0.6988(12)	0.056(8)
C17	0.746(4)	0.936(3)	0.2196(11)	0.099(10)
C18	0.562(3)	0.842(2)	0.1952(8)	0.084(8)
C19	0.485(4)	0.581(4)	0.8891(12)	0.106(9)
C20	0.280(4)	0.569(4)	0.8600(12)	0.098(10)

[i] Atoms C9*A*, C9*B*, C10*A*, and C10*B* were assigned an occupancy factor of 0.5 in order to model the ethylene group disorder. Isotropic displacement parameters were refined for these atoms.

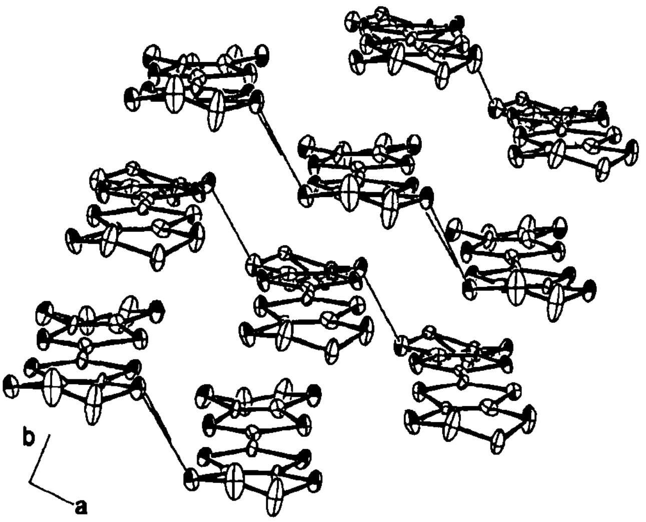

FIGURE 1 Perspective view of the BEDT-TTF donor molecule layer (*ab*-plane) in (BEDT-TTF)$_2$Cl$_2$SeCN. Intermolecular S···S contacts shorter than 3.6 Å are indicated with thin lines. Hydrogen atoms are omitted for clarity.

The same space group ambiguity with regard to the presence or absence of an inversion center exists for both compounds. While the structure is described here as non-centrosymmetric (space group $P1$, 365 variables, $R = 0.046$, $wR = 0.044$, $S = 1.59$) and crystallographically ordered with respect to the anion (see Figure 2, middle), this order may well be only local and possibly anisotropic (average space group $P\bar{1}$). In particular, it is assumed that the order holds over considerable repeat periods along the short *a*-axis chain direction, since the arrangement of two neighboring molecules in a tail-to-tail fashion, while keeping the Se—Se distance the same, would lead to strong intermolecular repulsion between colliding C—N groups (Figure 2, top). On the other hand, the lattice energy is almost the same if adjacent anion chains are oriented in parallel or antiparallel (Figure 2, bottom) fashion. However, no superlattice along the *b*-direction was observed. Ordered domains along the *b*- and *c*-directions are therefore expected to be of short range.

TABLE III Bond lengths (Å) and angles (°) in (BEDT-TTF)$_2$Cl$_2$SeCN.

Se—C0	1.729(10)	C7—C8	1.43(2)
Se—Cl1	2.416(7)	C9A—C10A	1.47(4)
Se—Cl2	2.445(7)	C9B—C10B	1.65(4)
N—C0	1.27(3)	S11—C13	1.79(2)
S1—C3	1.68(2)	S11—C11	1.79(2)
S1—C1	1.68(2)	S12—C11	1.67(2)
S2—C1	1.78(2)	S12—C14	1.69(2)
S2—C4	1.80(2)	S13—C15	1.75(2)
S3—C2	1.65(2)	S13—C12	1.81(2)
S3—C5	1.72(2)	S14—C12	1.72(2)
S4—C6	1.750(13)	S14—C16	1.73(2)
S4—C2	1.76(2)	S15—C13	1.73(2)
S5—C3	1.75(2)	S15—C17	1.77(2)
S5—C7	1.79(2)	S16—C14	1.76(2)
S6—C4	1.72(2)	S16—C18	1.79(2)
S6—C8	1.726(14)	S17—C15	1.73(2)
S7—C9B	1.73(3)	S17—C19	1.81(2)
S7—C5	1.78(2)	S18—C16	1.79(2)
S7—C9A	1.89(3)	S18—C20	1.82(2)
S8—C6	1.714(14)	C11—C12	1.32(2)
S8—C10A	1.76(4)	C13—C14	1.35(2)
S8—C10B	1.85(3)	C15—C16	1.32(3)
C1—C2	1.40(2)	C17—C18	1.32(3)
C3—C4	1.33(2)	C19—C20	1.23(3)
C5—C6	1.34(2)		

Table III continued.

C0—Se—Cl1	87.1(4)	C10A—C9A—S7	126(2)
C0—Se—Cl2	89.6(4)	C10B—C9B—S7	112(2)
Cl1—Se—Cl2	176.7(3)	C9A—C10A—S8	110(3)
N—C0—Se	172.3(15)	C9B—C10B—S8	107(2)
C3—S1—C1	97.1(9)	C13—S11—C11	93.5(9)
C1—S2—C4	93.2(9)	C11—S12—C14	97.6(8)
C2—S3—C5	95.4(9)	C15—S13—C12	96.2(8)
C6—S4—C2	93.9(7)	C12—S14—C16	96.3(9)
C3—S5—C7	101.7(9)	C13—S15—C17	105.1(10)
C4—S6—C8	104.6(9)	C14—S16—C18	98.2(8)
C9B—S7—C5	104.3(12)	C15—S17—C19	102.9(8)
C5—S7—C9A	94.0(12)	C16—S18—C20	98.1(9)
C6—S8—C10A	111.7(12)	C12—C11—S12	125.1(14)
C6—S8—C10B	100.9(10)	C12—C11—S11	119.5(14)
C2—C1—S1	122.9(13)	S12—C11—S11	114.9(10)
C2—C1—S2	121.9(14)	C11—C12—S14	124.8(14)
S1—C1—S2	115.2(10)	C11—C12—S13	122.8(14)
C1—C2—S3	122.2(12)	S14—C12—S13	112.2(10)
C1—C2—S4	121.0(13)	C14—C13—S15	132.1(13)
S3—C2—S4	116.7(9)	C14—C13—S11	114.8(14)
C4—C3—S1	119.9(14)	S15—C13—S11	113.0(11)
C4—C3—S5	124.3(14)	C13—C14—S12	119.0(13)
S1—C3—S5	115.6(10)	C13—C14—S16	123.7(14)
C3—C4—S6	132.8(14)	S12—C14—S16	117.2(9)
C3—C4—S2	114.4(14)	C16—C15—S17	130.1(13)
S6—C4—S2	112.8(11)	C16—C15—S13	115.0(14)
C6—C5—S3	118.9(13)	S17—C15—S13	114.7(9)
C6—C5—S7	127.8(13)	C15—C16—S14	120.2(15)
S3—C5—S7	113.3(12)	C15—C16—S18	126.9(15)
C5—C6—S8	128.1(11)	S14—C16—S18	112.6(12)
C5—C6—S4	114.8(11)	C18—C17—S15	117.4(14)
S8—C6—S4	117.1(7)	C17—C18—S16	135.3(14)
C8—C7—S5	125.7(15)	C20—C19—S17	118.7(19)
C7—C8—S6	117.1(10)	C19—C20—S18	130.5(19)

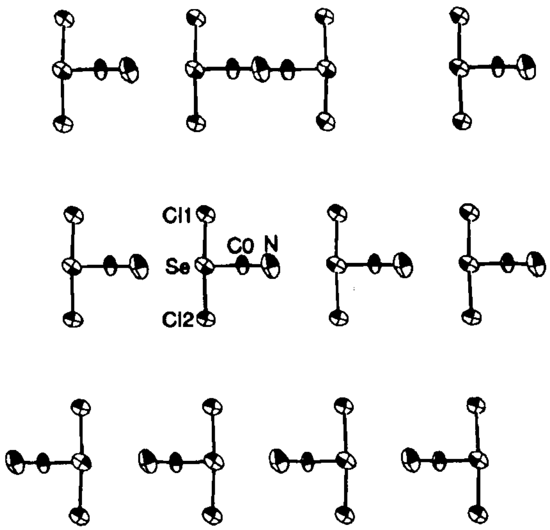

FIGURE 2 The anion layer in (BEDT-TTF)$_2$Cl$_2$SeCN, with the Se, Cl, and N atoms based on the actual structure analysis. The *a* axis is horizontal. The middle row shows the ordered row as required by the non-centrosymmetric space group *P*1. The top row shows the effect of inversion symmetric disorder within one anion chain, leading to C—N group collisions. No such collisions occur when an entire chain is inverted (bottom row).

Ordered linear chains of Cl_2SeCN^- anions with short non-bonded Se···N contacts have also been found in the tetramethylammonium salt.[6] The Se—Cl bond lengths of the anion in the title compound are essentially the same as in the $(CH_3)_4N^+$ salt, whereas the carbon atom is apparently shifted by ca. 0.1 Å towards the selenium atom, resulting in a shorter Se—C and a longer C—N bond length. However, because of the near-centrosymmetry in the structure and resulting strong correlations among the positional parameters, the carbon atomic position is not very reliably defined, and thus, these distances are not very accurate.

For comparison, the structure was also refined in the centrosymmetric space group $P\bar{1}$ with a disordered model. With 194 variables, agreement factors of $R = 0.052$, $wR = 0.051$, and $S = 1.798$ were obtained. Hamilton's *R*-value test[7] indicated that the ordered, non-centrosymmetric model was preferable at the 99% confidence level, as it was in the isostructural Br_2SeCN^- salt.

CONCLUSIONS

As in the case of the Br_2SeCN^- anion, oxidizing conditions in the presence of metal chloro-complexes readily convert the selenocyanate anion (divalent Se) to the *T*-shaped dichloroselenocyanate, Cl_2SeCN^-, which contains tetravalent Se. Its 2:1 salt with BEDT-TTF is isostructural with $(BEDT\text{-}TTF)_2Br_2SeCN$, and its physical properties, especially the conductive properties are virtually the same. The intermolecular S···S network suggests mainly one-dimensional interactions. Metallic conduction in quasi-one-dimensional systems is frequently suppressed by electron localization, thus leading to semiconducting behavior as in the present case.

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