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Synthesis, Structure, and Electrical Properties of $Ag_{1.2}$(2,5-dimethylthio-N,N´-dicyanoquinonediimine)

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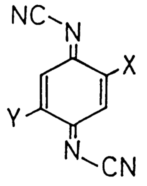
Several new DCNQI´s (N,N´-dicyanoquinonediimines) with methylthio groups are synthesized. One of their silver salts, the title compound, is metal down to 188 K. In this salt, a part of the Ag atoms are coordinated by the S and the inner N atoms.

Recently metal salts of DCNQI´s (1) have attracted a great deal of attention due to their highly conducting properties.[1,2] In particular, some Cu salts, Cu(1a)$_2$ and Cu(1b)$_2$, maintain their metallic properties down to liquid helium temperatures. In these salts, the N atoms of the CN groups coordinate to Cu, and Cu is in a mixed valence state.[3] As a result, the interchain interaction through the Cu atoms stabilizes the metallic state against one-dimensional instabilities. However, at low temperatures, Cu(1a)$_2$ undergoes a transition into a semiconducting phase under a pressure of as low as 100 bar.[4] In Cu(1b)$_2$, the critical pressure to a semiconducting phase rises up to 8 kbar, probably because the more bulky CH_3O group works so as to suppress the Jahn-Teller-like distortion of Cu.[5] In the present work, we attempted to prepare new DCNQI´s (1c-g) with more bulky CH_3S groups in order to realize a more stable metallic state. Unfortunately crystals of their Cu salts have not been obtained, but we have found that the Ag salt of 1c has a largely different crystal structure from those of the other known DCNQI salts. Its electrical resistivity and thermoelectric power are also reported.



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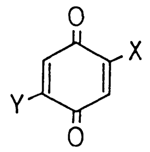

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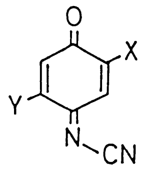

3

	X	Y
a	CH_3	CH_3
b	CH_3O	CH_3O
c	CH_3S	CH_3S
d	CH_3S	H
e	CH_3S	CH_3
f	CH_3S	CH_3O
g	CH_3S	Cl

The syntheses of the DCNQI´s were basically similar to Ref. 6. $TiCl_4$ (6 mmol) and bis(trimethylsilyl)carbodiimide (6.6 mmol) were succesively added to a 15 ml CH_2Cl_2 solution of the corresponding quinone (2c-g) (3 mmol).$^{7)}$ After an overnight reaction, petroleum ether was added, and the precipitate formed was filtered, dried in vacuo, and extracted with 30 ml $CHCl_3$. The extract was evaporated, and separated on silica gel flash chromatography using CH_2Cl_2. The initial red band yielded the unreacted quinone (2c-g), the subsequent violet bands yielded the partly reacted N-cyanoquinonemonoimines (3c-g), and the final yellow or violet band yielded the DCNQI (1c-g) (yield 3 - 5%). The products were identified by the spectroscopic methods.

Figure 1 summarizes the results of cyclic voltammogram. These DCNQI´s show two reversible waves, and are as good acceptors as tetracyanoquinodimethane (TCNQ). The CH_3S group is slightly more electron withdrawing than CH_3 or H. The redox potentials of 3 appear about midway between those of the corresponding DCNQI (1) and quinone (2).

Electrochemical reduction of 1c-g in the presence of $CuBF_4$ in acetonitrile gave only low-conducting powder. The direct reactions with CuI or copper wire were also unsuccessful. Electrochemical reduction of 1c in the presence of $AgBF_4$ in acetonitrile gave black plate-like crystals of $Ag_{1.2}$(1c), where the composition was determined from the Ag occupancy of the crystal structure (vide infra). Attempts to prepare alkali metal salts of 1c and the Ag salts of the other DCNQI´s were unsuccessful.

X-Ray single crystal structure analysis of $Ag_{1.2}$(1c) was carried out. Crystal data: orthorhombic, space group Pban, a = 16.926 (3), b = 7.123(1), c = 9.917(3) Å, V = 1195.6 (5) $Å^3$, and Z = 4. The final R value is 0.116 (by using 533 independent reflections) due to the disorder of the Ag atoms.

The crystal structure is largely different from those of the other known DCNQI´s (Fig. 2).$^{8)}$ The DCNQI molecules are stacked along the b axis with the inter-planer spacing of 3.3 Å, where a CH_3S part is located just above an NCN group, and the CH_3S and NCN parts are arranged alternately.

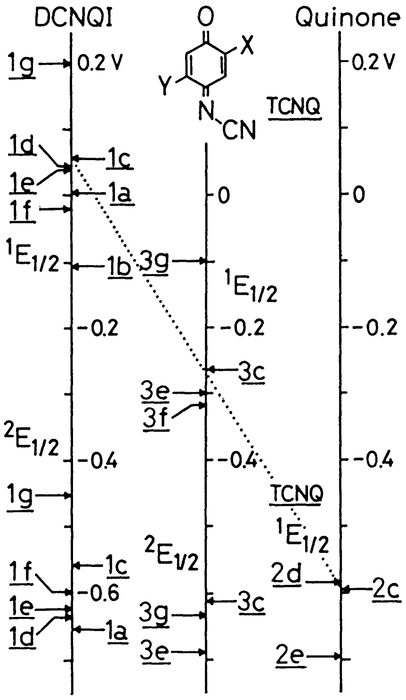

Fig. 1. Half-wave redox potentials(vs. Ag/AgCl reference electrode), measured in Bu_4NPF_6/acetonitrile at a Pt working electrode.

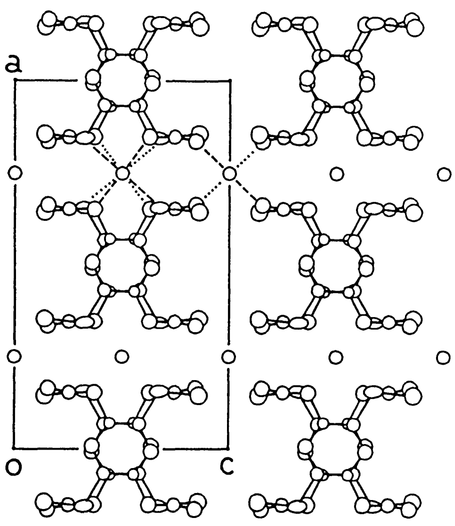

Fig. 2. Crystal structure of $Ag_{1.2}$(1c), projection along the b axis.

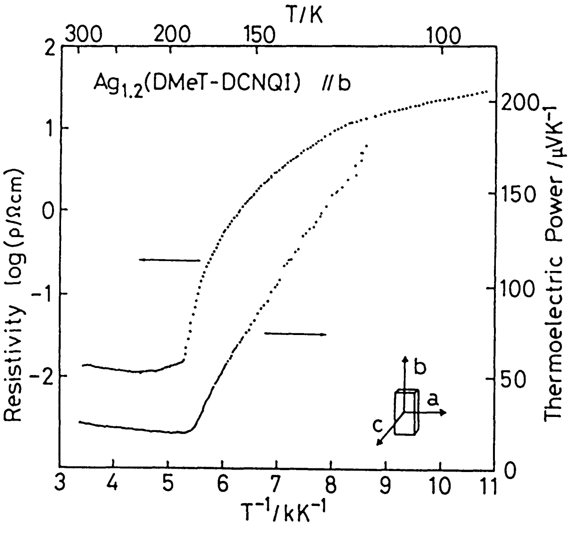

Fig. 3. Electrical Resistivity and thermoelectric power of $Ag_{1.2}$(1c) along the b axis.

There are two different kinds of Ag sites. One kind of the Ag sites is coordinated by the four S atoms of the CH_3S groups (d_{Ag-S} = 2.79 Å), and the four inner N atoms of the NCN groups (d_{Ag-N} = 2.98 Å and ∠S-Ag-N = 64°). 72 % of these sites are occupied by Ag. The other kind of Ag is tetrahedrally coordinated by the four outer N atoms of the NCN groups (d_{Ag-N} = 2.44 Å), similarly to the other known DCNQI salts. These sites are 46 % occupancy. From these Ag occupancies, the composition is determined to be $Ag_{1.18}$(1c). We found no evidence of the long-range order of the Ag atoms.

The electrical resistivity and the thermoelectric power along the b axis are shown in Fig. 3. The conductivity is about 100 Scm^{-1} at room temperature, and almost constant down to T_{MI} = 188 K, where occurs a metal-to-semiconductor transition. The rapid increase of the resistivity just below T_{MI} is similar to other DCNQI salts.[2)] The activation energy is 0.03 eV around 100 K. The thermoelectric power is positive in spite of an acceptor conductor, because the conduction band exceeds half filled. From the linear temperature dependence of the thermoelectric power in the metallic region, the bandwidth is estimated to be 0.30 eV, by assuming the one-dimensional tight-binding band. This value is slightly smaller than those of other DCNQI salts, 0.4 - 0.5 eV.[2)] The activation energy below T_{MI} is 0.05 eV.

The temperature dependence of the lattice constants (Fig. 4) shows an anomaly around 200 K. This suggests that the transition at T_{MI} is associated with some kind of structural change.

In conclusion, most characteristic of $Ag_{1.2}$(1c) is the coordination of S to Ag. The reason why alkali metals do not make similar crystals with 1c, is that "hard" alkali metals do not prefer such a coordination. Coordination of S to Cu also does not seem to be very preferable. The reason why the "unsymmetrical" DCNQI´s (1d-g) with only one CH_3S do not form similar Ag crystals, is regarded that the crystal structures of the 1c salt and the other DCNQI salts are largely different.

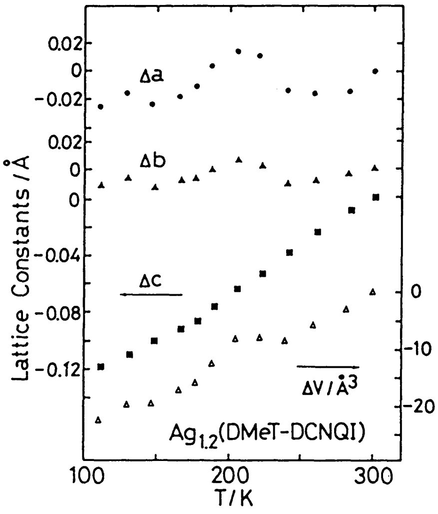

Fig. 4. Temperature dependence of the lattice constants of $Ag_{1.2}$(1c).

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