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Giral, C.S. Jacobsen, K. Bechgaard

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CHEMICAL PREPARATION AND PHYSICAL PROPERTIES OF A METALLIC ORGANIC CHARGE TRANSFER COMPLEX : HMTTF-TCNQ

P. DELHAES, S. FLANDROIS, J. AMIELL, G. KERYER

Centre de Recherches Paul-Pascal (C.N.R.S.), Université de Bordeaux I, 33405 Talence, France

E. TOREILLES, J. M. FABRE, L. GIRAL

Laboratoire de Chimie Structurale Organique (U.S.T.L.), 34060 Montpellier, France

C. S. JACOBSEN

Physics Laboratory III, Technical University of Denmark, DK 2800, Denmark

and

K. BECHGAARD

Chemistry Laboratory II, H.C. Oersted Institute, University of Copenhagen, DK 2100, Denmark

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Résumé. — Une nouvelle synthèse de l'hexaméthylènetétrathiofulvalène et de son complexe de transfert de charge avec le TCNQ est décrite. La variation thermique de la conductivité électrique confirme l'existence d'un maximum ($T_{\max} \simeq 75$ K) et deux transitions ($T_{c_1} = 49 \pm 1$ K, $T_{c_2} = 43 \pm 1$ K).

L'étude du paramagnétisme statique, dynamique (R.P.E.), et de la chaleur spécifique montre que T_{c_2} doit être associée à une distorsion de réseau sur la chaîne de HMTTF et qu'en outre celle-ci joue un rôle prédominant dans les phénomènes électroniques. La largeur de raie est reliée à l'existence d'interactions entre chaînes plus grandes que dans TTF-TCNQ en accord avec le comportement de la conductivité électrique.

Abstract. — A new chemical preparation of hexamethylenetetrathiofulvalenium and of the HMTTF-TCNQ charge transfer complex is described. The d.c. conductivity has been measured as a function of temperature; it shows a broad maximum ($T_{\max} \simeq 75$ K) followed by two transitions ($T_{c_1} = 49 \pm 1$ K, $T_{c_2} = 43 \pm 1$ K).

The static paramagnetism, E.P.R. and specific heat have been measured; they indicate that T_{c_2} must be associated with the appearance of a periodic lattice distortion of the HMTTF chains which (dominate observed behaviour). The line-width is determined by interactions between chains which are more efficient in this compound than in TTF-TCNQ, in agreement with the behaviour of the electrical conductivity.

1. Introduction. — As a contribution to the study of metallic organic charge transfer complexes we want to report the synthesis and the physical properties of a compound belonging to the TTF (tetrathiofulvalenium) family. The TTF-TCNQ charge transfer complex has been intensively studied but interest has recently spread to other similar complexes, in particular the selenium analogs, among them HMTSF-TCNQ which has been found to be conducting down to 1 K [1] and which is semi-metallic under pressure [2]. In order to get a better knowledge of the general behaviour of this class of organic materials it is therefore of considerable interest to study the sulphur analog : HMTTF-TCNQ.

2. Chemical preparation. — Hexamethylenetetrathiofulvalenium (HMTTF) has been synthesized from dithiocarbamate [3]. Two original ways are proposed, as outlined in table I, to obtain HMTTF which is later purified by multiple soxhlet extractions with dichloroethylen under argon. TCNQ was purified by gradient sublimation onto teflon (three times) and HMTTF-TCNQ crystals were prepared by slow cooling of chlorobenzene solutions saturated at 110 °C in quartz vessel.

By this procedure a simple salt similar to that recently described by Greene *et al.* [4] has been prepared.

TABLE I

3. Physical properties. — **3.1 ELECTRICAL CONDUCTIVITY.** — The absolute value at room temperature and the temperature variation of the d.c. electrical conductivity along the needle axis are similar to the data previously published [4] (Fig. 1). At around 75 K there is a broad conductivity maximum which is followed by two sharp transitions at $T_{c1} = 49 \pm 1$ K

FIG. 1. — Variation with temperature of the d.c. electrical conductivity versus T^{-1} ; the absolute d.c. conductivity at room temperature is $\sigma \approx 550$ ($\Omega \text{ cm}$) $^{-1}$. The insert shows how the relationship $\rho = a + bT^2$ is obeyed in the metallic phase, i.e. above 100 K.

and $T_{c2} = 43 \pm 1$ K, for falling temperature. Above the transitions a quadratic temperature dependence of the resistivity is observed as in other metallic charge transfer complexes [1, 2]. These measurements confirm that these crystals are of the same kind as those prepared by Greene [4].

3.2 STATIC SUSCEPTIBILITY. — The temperature variation of the static susceptibility obtained by Faraday's method is shown in figure 2. Below 30 K the susceptibility follows a Curie law: a plot of χ_{exp} versus T^{-1} gives a straight line whose slope is the Curie constant $C \approx 14.7 \times 10^{-4}$ emu.K/mole (corresponding to 3.9×10^{-3} paramagnetic centres per mole assuming $g = 2$ and $S = \frac{1}{2}$). The extrapolation to $T^{-1} \Rightarrow 0$ gives $\chi = -2.8 \times 10^{-4}$ emu/mole which is in good agreement with the diamagnetism calculated from Pascal's constants (-2.7×10^{-4} emu/mole) [5]. After subtracting the Curie part and the core diamagnetism from the observed susceptibility, the residual part is obtained. The temperature variation of the paramagnetism, although at first sight appearing normal, seems to show a change in slope at around 44 K if $\ln(\chi T)$ is plotted versus T^{-1} (Fig. 2).

FIG. 2. — Variation with temperature of the magnetic susceptibility. The experimental points (crosses) are given in the lower part of the figure. The intrinsic paramagnetism (dots) obtained after corrections for core diamagnetism and Curie paramagnetism are given in the middle part. The inset gives a plot of $\ln(\chi T)$ versus T^{-1} .

3.3 E.P.R. INVESTIGATION. — The experiments have been carried out on single crystals with a Varian X band spectrometer equipped with home made (below 78 K) and standard (78-400 K) thermal variation accessories.

From the structure determination [4] we know that this charge transfer complex crystallizes in the orthorhombic system. By rotation diagrams at 295 K we have checked that the g -factor and the line-width between inflexion points (S) of the unique line behave as second order tensors with the principal axes in agreement with the crystallographic axes. For the three defined positions we have studied the thermal variations of the EPR line between 5 and 400 K as indicated on figure 3. The labelling of the g -factor and line-width has been done following Greene's work [4]; without morphological indications the X and Z directions are indistinguishable: they have been attributed by analogy with Tomkiewicz *et al.*'s [6] experiments on TTF-TCNQ because of the similarities in behaviour except for the g -factor temperature variation (Fig. 3b).

FIG. 3. — Variation with temperature of the diagonal terms of the g -factor (●) and line width S (○) tensors: a) the magnetic field H_0 parallel to the Y axis; b) and c) H_0 is parallel to the Z and X axis and the microwave field H_1 parallel to the needle axis Y . Insert of figure c) mean values of $\bar{g}$ and $\bar{S}$.

The observed line-width is roughly Lorentzian in these two directions (X and Z) but slightly asymmetric, due to a small skin effect, in the Y direction.

3.4 SPECIFIC HEAT MEASUREMENTS. — The experiments have been carried out between 1.5 and 10 K with an adiabatic calorimeter. The sample was a pellet weighing around 100 mg placed on an alumina support as described elsewhere [7]. The specific heat of HMTTF-TCNQ is presented on figure 4 where we can see that just a usual cubic term appears which allows us to calculate the Debye temperature ($\theta_D = 86$ K). This result can be compared to the low temperature specific heat of TTF-TCNQ ($\theta_D = 89.5$ K) [8].

FIG. 4. — Variation with temperature of the specific heat C_p between 1 and 5 K plotted as C_p/T versus T^2 (the experimental error is about 5 to 10 %).

4. Analysis and interpretation. — **4.1 GENERAL REMARKS.** — The physical experiments carried out on this material have shown the sample quality. The d.c. conductivity is similar, even slightly better than in the previous investigation [4]. The observed Curie tail observed on the paramagnetism is small; the paramagnetic localized centres do not affect the g -value thermal variation except at very low temperatures (at $T = 10$ K the mean g -value is $\bar{g} \approx 2.0045$).

4.2 PHASE TRANSITIONS ANALYSIS. — The specific heat in the helium temperature range (Fig. 4) is characterized by the absence of a linear term which indicates a non magnetic ground state and confirms that a metal insulator transition has taken place at higher temperatures on the two chains. The g -factor anisotropy (Fig. 3) gives a first insight into this phenomenon. The large value detected below 100 K indicates that the paramagnetism is predominantly on the HMTTF chains determined at low temperatures.

As shown in the insert of figure 3 the mean $\bar{g}$ value ($\bar{g} = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$) reaches a maximum around 43 K ($\bar{g} = 2.0077$) which is near to the accepted $\bar{g}$ value for TTF⁺ in solution ($\bar{g} = 2.00838$) [9]. This result suggests the occurrence of a Peierls distortion on HMTTF chains. This analysis is supported by the thermal variation of the paramagnetism which decreases strongly below 44 K (Fig. 2). It seems to us, therefore, that the paramagnetism is also mainly governed by the characteristics of HMTTF chains.

4.3 LINE-WIDTH BEHAVIOUR AND 3D INTERACTIONS. If we now examine the line-width thermal variations we conclude that the three principal values behave similarly as in TTF-TCNQ [4] with a maximum around 70 K. The line-width anisotropy is characterized by the ratio S_{xx}/S_{yy} or S_{xx}/S_{zz} which increases at low temperatures but is always lower than two. This is in agreement with Yafet's theory [10] for conduction electrons in anisotropic solids when the motional narrowing is complete. This picture is confirmed by

the similar thermal variations of the d.c. conductivity and S_{yy} (see Fig. 1 and insert of Fig. 3c) which increase identically from room temperature down to the respective maxima temperatures. From an argument, given by T. D. Schultz and quoted in [6], the relaxation processes are more and more efficient when the departure from the one dimensionality of the electronic system becomes larger. The relaxation times T_1 and T_2 ($T_2 \propto T_1$) are shorter and the line-widths larger when the interchain electronic coupling is stronger. In this compound the line-width at a given temperature is twice as large as in TTF-TCNQ, which indicates larger 3-D couplings. However the thermal variation of d.c. conductivity between T_{c1} and T_{max} (Fig. 1) indicates resistive fluctuations as already pointed out by Horn and Rimai for TTF-TCNQ [11].

4.4 CONCLUSION. — A comparison with the properties of HMTSF-TCNQ can be performed in view of the similar crystallographic structure. Above 90 K the observed thermal variation of the paramagnetism is parallel to that of HMTSF-TCNQ [12] with a slightly larger value for HMTTF ($+1.2 \times 10^{-4}$ emu CGS/mole) but no Landau diamagnetism occurs. This result supports the similarities of the conductivity and thermopower behaviour, as pointed out by Greene *et al.* [4].

In conclusion this investigation has shown that the magnetism of HMTTF chains is predominant and that these chains undergo a Peierls transition at 43 K. In such a picture the anomaly of conductivity detected around 49 K might be attributed to the TCNQ chains distortion; it seems therefore that Greene's assumption [4] that the conductivity in these complexes could be dominated by only one chain is confirmed. However the amount of charge transfer has yet to be known; therefore a detailed and quantitative understanding of these transitions awaits for a more complete crystallographic investigation.

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