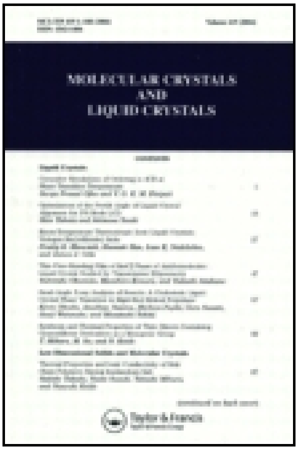


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Chemical and Physical Properties of Cation Radical Salts of BEDT-TTF

Gunzi Saito [a] , Toshiaki Enoki [b] , Mototada Kobayashi [b] , Kenichi Imaeda [b] , Naoki Sato [b] & Hiroo Inokuchi [b]

[a] Inst. Solid State Physics, Univ. of Tokyo, Tokyo, Japan

[b] Inst. Molecular Science, Okazaki, Japan

Version of record first published: 17 Oct 2011.

To cite this article: Gunzi Saito , Toshiaki Enoki , Mototada Kobayashi , Kenichi Imaeda , Naoki Sato & Hiroo Inokuchi (1985): Chemical and Physical Properties of Cation Radical Salts of BEDT-TTF, Molecular Crystals and Liquid Crystals, 119:1, 393-400

To link to this article: http://dx.doi.org/10.1080/00268948508075189

Mol. Cryst. Liq. Cryst. 1985, Vol. 119, pp. 393-400
0026-8941/85/1194-0393/$15.00/0

Printed in the United States of America

CHEMICAL AND PHYSICAL PROPERTIES OF CATION RADICAL SALTS OF BEDT-TTF

GUNZI SAITO, Inst. Solid State Physics, Univ. of Tokyo, Tokyo,
TOSHIAKI ENOKI, MOTOTADA KOBAYASHI, KENICHI IMAEDA, NAOKI SATO,
HIROO INOKUCHI, Inst. Molecular Science, Okazaki, Japan.

Abstract Extension of TTF skeleton by alkylthio groups makes the donors superior even to TMTSF concerning ionization potential, polarizability, and on-site Coulomb repulsion. Furthermore, due to the presence of the outer sulfur atoms, BEDT-TTF can form two-dimensional network by side-by-side arrangement in the complexes. The balance between the face-to-face and side-by-side interactions results in a variety of polymorphic complexes. We have been studying chemical, physical, structural, and designing works of cation radical salts of BEDT-TTF compounds. (BEDT-TTF)$_2$ClO$_4$(TCE)$_{0.5}$ shows metallic character down to 1.4K with phase transitions at ca.170K and 15K in electrical conductivity. The ESR and static magnetic studies show additional phase transitions. Different temperature dependence of magnetic properties was observed in the relaxed and quenched samples of this salt. A magnetic phase below 20K was formed by relaxing the salt at high temperature.

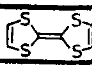
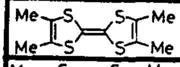
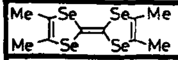
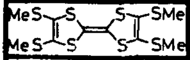
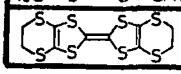
INTRODUCTION

It is well established that to obtain superconductor from organic metal, it is essential to suppress the Peierls transition at first. In order to do that, one has to destroy the nesting of the Fermi surface of the low-dimensional organic metal. Up to now, there are two tactics for that purpose. The first one is the introduction of non-periodicity. Many chemists synthesized unsymmetric donors and acceptors to modify the Fermi surface. Also the introduction of disorder and defect into the lattice has been performed to get nonperiodic surface. But unfortunately, these methods are very difficult to controle, because we still don't know what kind of and how much nonperiodicity we need to suppress the Peierls transition. The second tactics are the increase of dimensionality. Many physicists applied pressure to organic metals to obtain organic superconductors. And some cases they succeeded to wipe out the Peierls transition. This is a physical method to increase the interchain interaction. The last one is the chemical modification to increase dimensionality and we took this method. The first candidate was the extension of TTF skeleton by chalcogenide atoms.

WHY BEDT-TTF?

By extension of TTF skeleton by chalcogenide atoms, one may expect increase of band width, interchain interaction, and polarizability and also decrease of on-site Coulomb repulsion. All these factors enhance the metallic character, and especially increased interchain interaction is correponding to the increased dimensionality. Table 1 shows gas phase(adiabatic) ionization potential(I_g^a, eV), estimated polarizability(α, $10^{-30}m^3$) using ionization potential in solid state and I_g^a, and the difference of the first and the second oxidation potential(ΔE, V) which is a measure of the on-site Coulomb repulsion of donors in TTF family.[1] By addition of four sulfurs to TTF; BEDT- and TTM-TTF, ionization potential decreases by 0.1-0.2eV to the value of TMTSF. While, the polarizability increases more than twice of that of TTF, and 23-28% increase than that of TMTSF. The on-site Coulomb repulsion decreases considerably by that extension. ΔE values of BEDT- and TTM-TTF are almost half of that of TMTSF. Therefore, BEDT- and TTM-TTF are better donors than TMTSF as long as these parameters concern.

TABLE I On-site Coulomb repulsion($\propto\Delta E$), ionization potential (I_g^a), and polarizability(α).

DONOR	ΔE	I_g^a	α
	0.36	6.4	16.5
	0.49	6.03	21.0
	0.39	6.27	30.7
	0.19	6.29	39.4
	0.24	6.21	37.9

The structural study of the neutral donor indicates that the extension of TTF skeleton makes the donor very nonplanar.[2] Both donors are distorted about the central tetrathioethylene group pointing out the disadvantage of using TTM- and BEDT-TTF molecule in the study of organic metals, because of the inconvinence for the formation of face-to-face segregated columns. However, it was discovered that the formation of CT complexes makes both molecules flat except the terminal methyl or ethylene groups. In the case of BEDT-TTF complexes, nonplanarity of the outer ethylene groups is not so tremendous compared with that of the outer methyl groups in TTM-TTF where protruding methyl groups prevent compact packing of the donor stack in complexes. Therefore we need capping of the outer sulfur atoms to have appropriate stacking.

The most important characteristic of BEDT-TTF compounds is the compromise between the face-to-face interaction and the side-by-side interaction of BEDT-TTF molecules.[3] The outer sulfurs tend to form sulfur-to-sulfur network along the short molecular axis. High electrical conductivity can be achieved along this direction as well as along the stacking axis due to the face-to-face interaction where the nonplanarity of the outer ethylene groups prevents good overlap. As a result, the balance between the face-to-face and side-by-side interactions and flexibility of the outer ethylene groups yield a variety of polymorphic complexes depending on the solvents, counter anions, and other experimental conditions.

With perchlorate, BEDT-TTF gives four complexes, the first two are 2:1 salts which include solvent(1,1,2-trichloroethane(TCE) and dioxane), next is 3:2 salt and the fourth is a blue salt without any data of physical properties because it is very explosive. We show some magnetic properties of two salts; $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$ and $(BEDT\text{-}TTF)_3(ClO_4)_2$, to understand their phase transitions and their metallic character in order to explore the next designing work.

PHYSICAL PROPERTIES

$(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$···This salt does not show Peierls transition at all. The room temperature conductivity is 25Scm^{-1}, and 1000Scm^{-1} at 15K, below that resistivity increases a little bit(Curve a in

Figure 1). But some cases we observe resistivity increase between 250K and 170K when the cooling rate is slow(Curve b in Figure 1), and then the upturn at low temperature becomes more noticiable. These observations suggest that there are at least two phase transitions, one is around 180K and the other is below 20K. By diffuse X-ray study, the phase transition around 180K was confirmed by observing satellite spot (1/2, 0, 1/2) growing below 200K, and was considered to be due to an orientational order-disorder of TCE.[4] A preliminary X-ray study at 150K revealed, however, that TCE and ClO_4 molecules are still disordered, while the terminal ethylene groups are partly frozen.

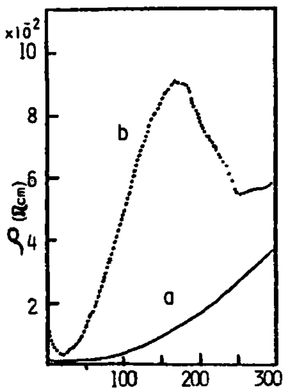


FIGURE 1 Resistivity vs temperature of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$.

The metal-metal phase transition observed in Curve b in Figure 1 suggests that the origin of the phase transition is not a molecular displacive one, but more conceivably an ordering of TCE or ClO_4 or freezing of the ethylene groups. Since these molecules and groups are arranged along b* axis, ESR and magnetic results along this direction will be mensioned mainly.

The spin-orbit coupling is the greatest along b* axis(g=2.013) and in the ac-plane g values are the same as that of free electron, indicating that the carrier of conduction is hole and locates on BEDT-TTF molecules. g-Values do not show any anomaly to 2K, reflecting the non-displacive nature of the phase transition of this compound(Figure 2). The line width along b* is 34 gauss at room temperature and decreases gradually with temperature decreases(Figure 2). There is an inflection point around 110K, which does not agree with the phase transition in conductivity. This behavior cannot be explained now, but the temperature dependence is very similar to that observed in $(TMTSF)_2PF_6$ and here also Elliott relation cannot

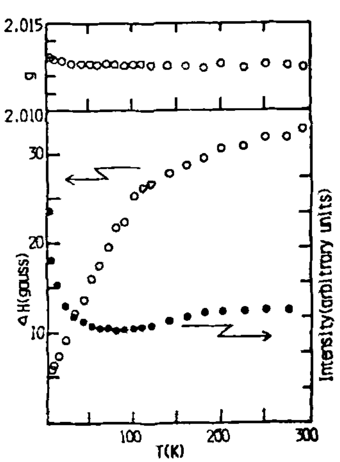


FIGURE 2 Temperature dependences of g-values, line width(ΔH), and intensity of quenched (BEDT-TTF)$_2$ClO$_4$(TCE)$_{0.5}$.

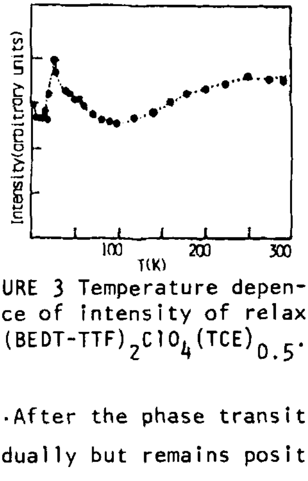


FIGURE 3 Temperature dependence of intensity of relaxed (BEDT-TTF)$_2$ClO$_4$(TCE)$_{0.5}$.

be applied.[5] Intensity is almost flat down to 180K(Figure 2). This temperature is corresponding to the phase transition in conductivity. At lower temperatures, there is some Curie-like paramagnetic signal which conceals the low temparature phase transition. Those are the results on quenched sample.

By relaxing the sample down to 20K(cooling rate=5-10K/hr), a different temperature dependence of intensity was observed especially at low temperature(Figure 3). Although the Curie-like signals interfere the low temperature feature considerably, this figure indicates that some amount of paramagnetic species became diamagnetic below 20K by relaxing.

Static magnetic susceptibility measurement shows the phase transition more precisely. There are possible phase transitions at 175, 90, 50, and 15K on quenched sample(cooling rate=5K/min)(Figure 4a).After the phase transition at 175K, the magnitude decreases gradually but remains positive down to 2K. This emphasizes that the quenched (BEDT-TTF)$_2$ClO$_4$(TCE)$_{0.5}$ is metal in the whole temperature range measured.

To investigate the effect of phase transition around 175K alone, we have relaxed(5K/hr) the complex only down to 160K, then

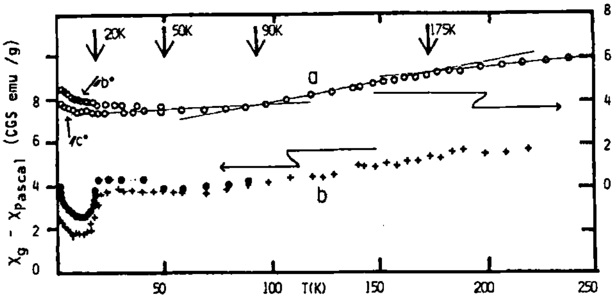


FIGURE 4 Magnetic susceptibility of quenched (Curve a) and relaxed(Curve b) $(BEDT\text{-}TTF)_2ClO_4\text{-}(TCE)_{0.5}$.

quenched(5K/min) to 2K. After that, susceptibility was measured up to 90K(indicated by shaded circles Figure 4b, warming rate=1K/min). Then the sample was quenched to 2K(5K/min) and χ values were measured again up to high temperature(indicated by cross Figure 4b, warming rate=1K/min). The behavior at low temperature ≲20K changed drastically, that some spins were killed and the density of states decreased by relaxing the sample above 160K. This feature is quite similar to that observed in ESR measurement. The hysteresis below 50K indicates that warming the relaxed sample up to 90K makes it more and more diamagnetic.

Table 2 shows a summary of the 2:1:0.5 complex. First of all

		Phase Transition (K)			
Conductivity	σ_{RT}=25Scm^{-1}, metal≥1.4K, σ_a/σ_c~1	200~170			15
Diffuse X-ray	satellite (0.5, 0, 0.5)	200~			
X-ray (at 150K)*	-CH_2-CH_2- partly frozen, ClO_4, TCE disordered				
ESR g	2.0125(b*), 2.0023(ac)				
ΔH	33G(b*), 26G(ac)		~110		
I (Q)		180			
(R)					20
Static χ (Q)	$4t_{\parallel}$=0.084eV, metal≥2K	175	90	50	20
(R)				50	20

Origin of Phase Transition -CH_2-CH_2- TCE? ClO_4? magnetic ordering

Phase Transition metal — metal — metal — metal — semicon

TABLE 2 Summary of phase transition of $(BEDT\text{-}TTF)_2ClO_4(TCE)_{0.5}$.

(Q) :quenched sample
(R) :relaxed(≥160K) sample
* :Prof. H. Kobayashi, private communication.

it may be emphasized that our experiments indicate that the relaxing this BEDT-TTF salt above 160K induces the magnetically ordered state at low temperature below 20K. We suppose the phase transition above 160K is due to the freezing of ethylene vibration. We also suppose that the phase transition around 50K is ascribed to the order-disorder of ClO_4 as in the case of TMTSF salt. If so, above experiments lead that this perchlorate motion is strongly connected with the freezing of ethylene vibration. The freezing of ethylene vibration forces to order perchlorate ions, and the ordering of the ions may be a trigger of the metal-semiconductor transition around 20K. The hysteresis below 50K suggests that the perchlorate motion is also associated with the transition at ca.90K, maybe this is order-disorder of TCE. Or another explanation of the hysteresis is that more perchlorate ions become ordered state by annealing. If we can relax the salt perfectly, we may know the nature of this metal-semiconductor transition in detail. Anyway we can say at this stage that the ground state of this salt is magnetically ordered one, and these three possible phase transitions caused by motional freezing cannot make this salt insulator, maybe due to strong two-dimensionality.

As a matter of fact, the assignment of the origins of these phase transitions is conjectual, and we need precise X-ray study at low temperatures and also works on deutrated compounds to confirm the above assignment.

$(BEDT\text{-}TTF)_3(ClO_4)_2$···The conductivity shows rather sharp Peierls transition at 170K,[6] and we also experienced gradual resistivity anomaly around 200K in this salt. g-Values exhibit drastic change below 200K, which resembles to that observed in $(BEDT\text{-}TTF)_3(ReO_4)_2$ by IBM group.[7] This is an evidence of the structural displacive nature of this transition(Figure 5). Line width displays sharp drop at 170K corresponding to the Peierls transition, and a weak anomaly around 55K. The intensity shows weak anomaly around 60K also(Figure 5). The inflection point at 155K is slightly lower than those observed in conductivity and line width. The static magnetic susceptibility points out the Peierls transition clearly at 170K(Figure 6). The activation energy below this transition is 620-630K. By relaxing this compound down to 160K, we have observed slight magnetic change below 45K, but with other samples we did not see any change at all. We suppose that there are two phase transitions above 160K, one is a aharp Peierls transition and the other is the freezing of ethylene vibration. This freezing may be not connected with the phase transition around 50K, presumably this is due to order-disorder of perchlorate ions. The molecular motions of these two parts are more independent than the case of solvated 2:1 complex.

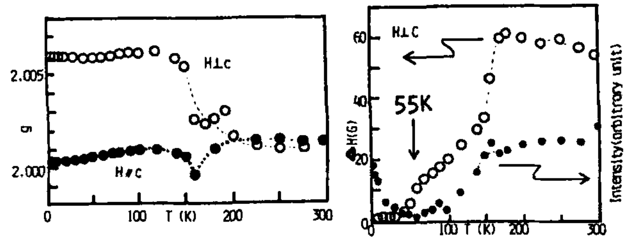


FIGURE 5 Temperature dependences of g-values, line width(ΔH), and intensity of $(BEDT\text{-}TTF)_3(ClO_4)_2$

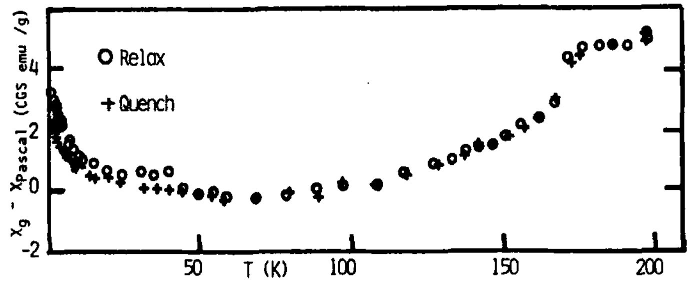


FIGURE 6 Magnetic susceptibility of $(BEDT\text{-}TTF)_3(ClO_4)_2$. H⊥c

REFERENCES

1. N. Sato, G. Saito, and H. Inokuchi, Chem. Phys., 76, 79 (1983).
2. a. H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, Mol. Cryst. Liq. Cryst., 107, 33 (1984). b. C. Katayama, J. Tanaka, and G. Saito, unpublished result.
3. G. Saito, T. Enoki, K. Toriumi, and H. Inokuchi, Solid State Commun., 42, 557 (1982).
4. S. Kagoshima, J. P. Pouget, G. Saito, and H. Inokuchi, Solid State Commun., 45, 1001 (1983).
5. H. J. Pedersen, J. C. Scott, and K. Bechgaard, Solid State Commun., 35, 207 (1980).
6. H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, Chem. Lett., 1984, 179.
7. K. Carneiro, J. C. Scott, E. M. Engler, Solid State Commun., 50 477 (1984).