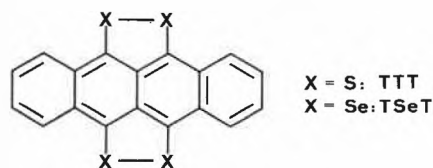


Progress in the Chemistry and Physics of the Organic Charge-Transfer Metals «TSeT·Br_{0.5}» and «TSeT·Cl_{0.5}»: Very High Electrical Conductivities under Pressure**

Bruno Hilti*, Carl W. Mayer, Ernst Minder, Kurt Hauenstein, Jürgen Pfeiffer, and Marcel Rudin

Abstract: On improved samples of the tetraselenotetracene derivatives TSeT·Br_{0.5} and TSeT·Cl_{0.5} we have obtained $\rho(4\text{K}, 8\text{kbar})/\rho(295\text{K}, 1\text{bar})$ ratios of $1.3 \cdot 10^{-3}$ and $1.7 \cdot 10^{-3}$, respectively. This corresponds to a resistivity $\rho(4\text{K}, 8\text{kbar})$ of $5 \cdot 10^{-7} \Omega \text{ cm}$ for TSeT·Br_{0.5} and $6.5 \cdot 10^{-7} \Omega \text{ cm}$ for TSeT·Cl_{0.5}. These are of the lowest non-superconductive resistivities ever observed in organic compounds.

The chalcogenated naphthalenes TTT (5,6,11,12-tetrathiotetracene) and TSeT (5,6,11,12-tetraselenotetracene) were successfully used as electron donors for the preparation of highly conducting charge-transfer salts from a very early stage in the search for organic metals and superconductors.



Thus, (TTT)₂I₃, discovered at about the same time by three research groups^[1-3], still holds the record for the highest electrical conductivity at room temperature with a value of $\sigma_{RT} = 4000 \Omega^{-1} \text{ cm}^{-1}$.

TSeT·Cl_{0.5}^[4] and TSeT·I_{0.5}^[5] were among the first organic compounds to be stabilized in a metallic state (state II) down to the lowest temperature investigated (0.1 K) by application of a hydrostatic pressure.

Under pressure the organic metals TSeT·X_{0.5} (X = Cl, Br, I) convert at room

temperature to a second metallic state, designated as state II (Fig. 1). When cooled in this state, the resistivity upturn observed around 30 K with the samples in state I (Fig. 2) is suppressed as shown in Fig. 3.

Whilst these two features, i.e. conversion from metal state I to metal state II upon application of pressure and the accompanying suppression of the metal-semiconductor transition around 30 K, proved to be inherent properties of these materials, the temperature dependence of the electrical resistivities in the range below 80 K were shown to be extrinsic step by step.

Work to improve the quality of these complexes with the hope of thereby achiev-

ing superconductivity has gone on for years at Ciba-Geigy and also in the group of Shchegolev.

By reducing the residual pressure in the gas phase preparation of TSeT·I_{0.5}, we were able to diminish considerably the admixture of I₃⁻ into the iodide anion columns of the TSeT·I_{0.5} crystals^[6], resulting in a lowering of the resistivity ratio $\rho_{\text{min}}/\rho_{RT}$ from 0.25 to 0.1.

The electrical properties of TSeT·Br_{0.5} and TSeT·Cl_{0.5}, originally prepared by chemical oxidation methods, were improved drastically by the use of the electrochemical crystallization method^[7, 8]. Further decisive progress towards the preparation of TSeT-halogen complexes with intrinsic solid state properties was initiated by the Russian group^[9] which first observed their extremely high sensitivity to halogen admixtures.

Experimental

We have now prepared high quality TSeT by keeping contamination by sulfur within each step of the synthesis^[10] below our present recording threshold of the X-ray fluorescence analysis, i.e. below a few ppm. This was necessary because TSeT itself reacts with sulfur impurities in the last step of the synthesis, resulting in the substitution of the selenium atoms to a various degree, i.e. in an exchange of one to four Se against S.

Crystals of TSeT·Br_{0.5} and TSeT·Cl_{0.5} were grown by electrocrystallization in the constant voltage mode, the current being of the order of about 0.1 μA . Resistivity measurements were performed with direct current in the four probe arrangement. Crystals of approximate size $2.5 \times 0.03 \times 0.03 \text{ mm}^3$ were mounted on four gold wires of 15 μm thickness and contacted with Pt-paste Degussa 308. The crystal holder was positioned in the Be-Cu high pressure clamp cell so that the needle-shaped crystals were oriented along the axial direction of the cell. As pressure transmitting medium silicon oil Merck Type 350 was used.

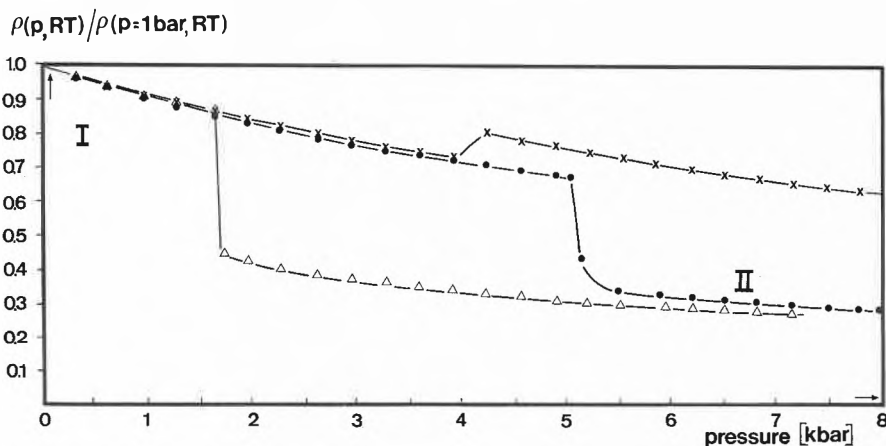


Fig. 1. Normalized electrical resistivity of tetraselenotetracene derivatives at room temperature (RT) as a function of pressure (p): TSeT·Br_{0.5} — \triangle —, TSeT·Cl_{0.5} — \bullet —, TSeT·I_{0.5} — \times —.

* Correspondence: Dr. B. Hilti
Central Research Laboratories
Ciba-Geigy AG
CH-4002 Basel

** Acknowledgements: We thank Dr. P. Kriemler and Dr. D. Müller for the recording of the numerous mass spectra and Dr. J. Pavel for the elaboration of X-ray fluorescence methods to determine trace impurities of sulfur in a selenium matrix. We also thank Mr. M. Bürkle and Mr. B. Sigrist for their experimental assistance.

Results

In Fig. 2 we show the temperature behaviour of the electrical resistivity at normal pressure of $TSeT \cdot Cl_{0.5}$ and $TSeT \cdot Br_{0.5}$. Whereas a relatively minor drop of the resistivity between 16 K and 4 K was reported by Shchegolev et al.^[7] for $TSeT \cdot Cl_{0.5}$ and none at all has appeared in the literature up to date for $TSeT \cdot Br_{0.5}$, both our newly prepared complexes now reveal a marked drop of the resistivity in this temperature range. Around 16 K also a pronounced hysteresis on cycling the temperature could be observed, eventually indicating a phase transition.

Measurements on samples in state II (Fig. 1) with a starting pressure of 8 kbar resulted in the lowest non-superconducting resistivities ever observed in an organic compound (Fig. 3). Thus, $\rho(4K, 8kbar)^{[11a]}$ for $TSeT \cdot Br_{0.5}$ is $5 \cdot 10^{-7} \Omega cm$ and for $TSeT \cdot Cl_{0.5}$ $6.5 \cdot 10^{-7} \Omega cm$ ^[11b]. Whilst hitherto $\rho(4K, 8kbar)/\rho(RT, 1bar)$ ratios of the order of 10^{-2} for $TSeT \cdot Cl_{0.5}$ ^[7] and of $4 \cdot 10^{-2}$ for $TSeT \cdot Br_{0.5}$ ^[8] were obtained, the corresponding ratios for the new samples are now as low as $1.7 \cdot 10^{-3}$ and $1.3 \cdot 10^{-3}$, respectively.

Further work is needed to find out the nature of the phase transition between 16 K and 4 K at normal pressure and to clarify its connection to the phase transition of state I to state II at room temperature under pressure.

Also, it must be considered as still uncertain, whether we have already reached the «ultimate» state of purity to see the truly intrinsic low temperature behaviour of these complexes (superconductivity?).

Received: January 14, 1986 [FC 52]

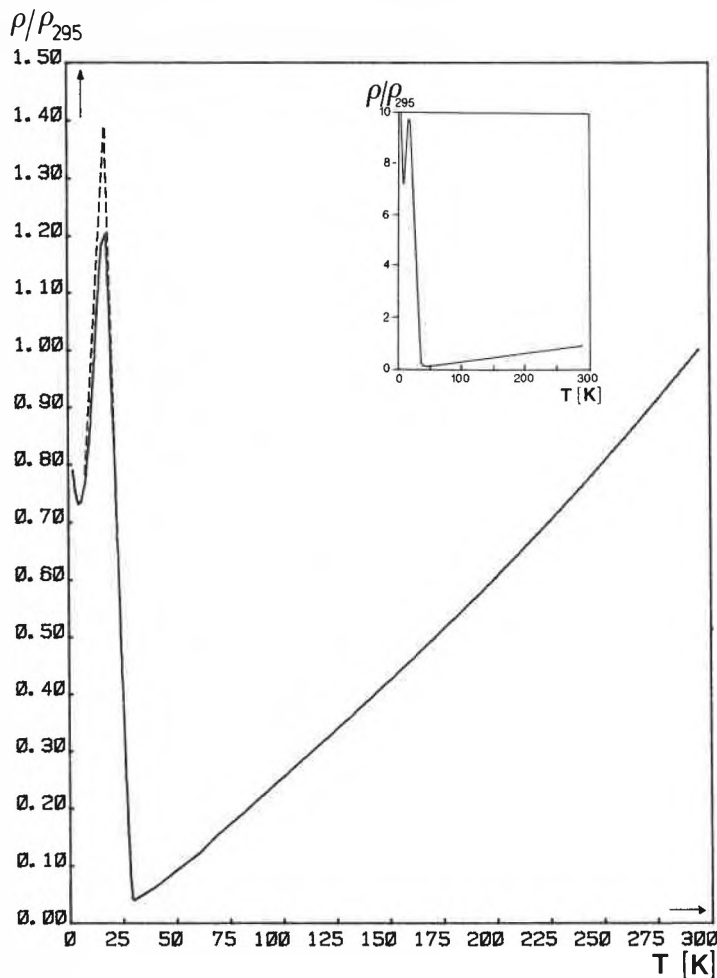


Fig. 2. Electrical resistivity normalized to the value at room temperature of $TSeT \cdot Cl_{0.5}$: cooling —, heating cycle — —. Insert: normalized electrical resistivity of $TSeT \cdot Br_{0.5}$.

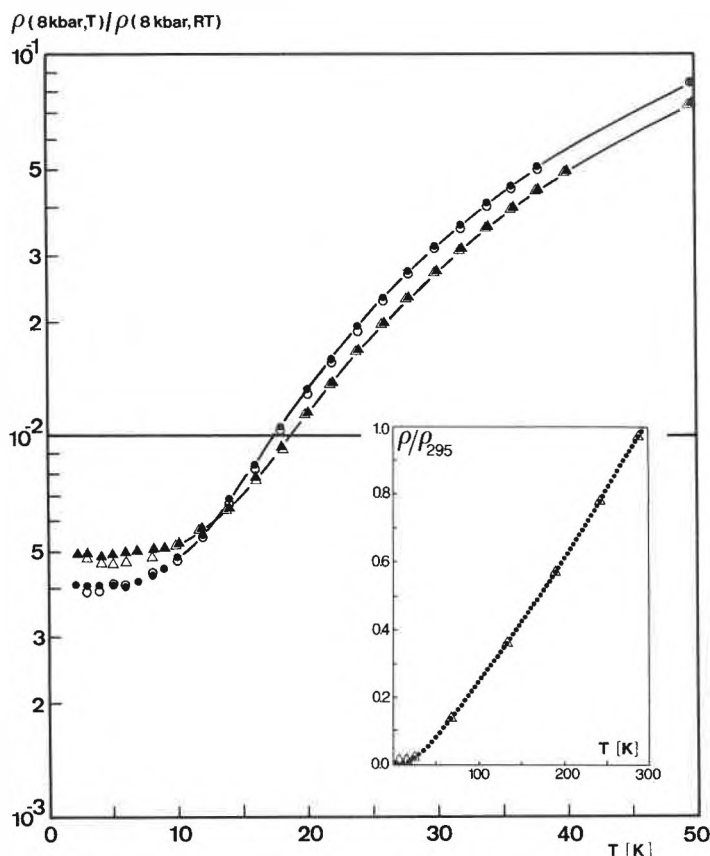


Fig. 3. Electrical resistivity under pressure normalized to the value at room temperature of $TSeT \cdot Br_{0.5}$: —●— cooling, —○— heating; $TSeT \cdot Cl_{0.5}$: —▲— cooling, —△— heating. Insert: the entire temperature range for the samples in the state II ($TSeT \cdot Br_{0.5}$ ●●●, $TSeT \cdot Cl_{0.5}$ △△△).

[1] L. I. Buravov, G. I. Zvereva, V. F. Kaminskii, L. P. Rosenberg, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev, E. B. Yagubskii, *J. Chem. Soc. Chem. Commun.* (1976) 720.
 [2] L. C. Isett, E. A. Perez-Albuerne, *Solid State Commun.* 21 (1977) 433.
 [3] B. Hilti, C. W. Mayer, *Ger. Offen.* 2 641 742 (24.03.77); *Swiss Appl.* 12230/75 (19.09.75); *Chem. Abstr.* 86 (1977) 181 613w.
 [4] S. P. Zolotukhin, V. F. Kaminskii, A. I. Kotov, R. B. Lubovskii, M. L. Khidekel, R. P. Shibaeva, I. F. Shchegolev, E. B. Yagubskii, *Pis'ma Zh. Eksp. Teor. Fiz.* 25 (1977) 474.
 [5] D. Jerome, A. Mazaud, M. Ribault, K. Bechgaard, *J. Phys. Lett.* 41 (1980) 95.
 [6] P. Delhaes, C. Coulon, S. Flandrois, B. Hilti, C. W. Mayer, G. Rihs, J. Rivory, *J. Chem. Phys.* 73 (1980) 1452.
 [7] P. A. Konovich, V. N. Laukhin, S. I. Pesotskii, I. F. Shchegolev, A. G. Khomenko, *JETP Lett.* 37 (1983) 92.
 [8] C. Weyl, L. Brossard, S. Tomič, D. Mailly, D. Jerome, B. Hilti, C. W. Mayer, *Mol. Cryst. Liq. Cryst.* 120 (1985) 263.
 [9] A. V. Zvarykina, V. N. Laukhin, E. E. Yurchakovich, E. B. Yagubskii, *Sov. Phys. JETP* 56 (1982) 446.
 [10] For details of the synthesis of $TSeT$, see: B. Hilti, C. W. Mayer, G. Rihs, *Helv. Chim. Acta* 61 (1978) 1462.
 [11] a) The actual pressure at 4 K is of the order of 3 kbar; b) $\rho(RT)$ for copper is about $2 \cdot 10^{-6} \Omega cm$.