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Highly Anisotropic Molecular Solids

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The physicochemical properties of quasi-one-dimensional crystals formed by charge-transfer complexes, radical-ion salts, and coordination and organometallic compounds are examined. The characteristics of the electrophysical, optical, and mechanical properties of these compounds due to the crystal structure and the nature of the movement of the electrons and (or) holes in them are discussed.
The bibliography includes 230 references

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I. INTRODUCTION

The development of the physics and chemistry of the solid state involves at the present stage the study of new classes of substances. The greatest advances are associated with the investigation of low-dimensional molecular solids—quasi-one-dimensional and quasi-two-dimensional. By quasi-one-dimensional systems, one understands systems exhibiting a high anisotropy of their physical properties: electrical resistance, magnetic susceptibility, reflection coefficient, Young's modulus, and others. The electrons in such systems can move mainly along one direction (filament) crossing from one filament to another only in rare instances either as a result of jumps or by tunnelling. Such systems are attractive because one can neglect to a first approximation the interaction between the filaments and one can consider one-dimensional movement for which there exist a whole series of many-particle models susceptible to exact solution.

The problem of quasi-one-dimensional systems arose after the publication of the interesting although erroneous study by Little[1]. This was associated with the problem of high-temperature superconductivity, namely the possibility of the operation of the exciton—electron mechanism of superconductivity. Little put forward a specific version of this mechanism (known as the Little model) comprising a polymeric highly conducting organic linear molecule containing side chains—monomers with a high polarisability. On the basis of the one dimensional model, Little applied the Bardeen—Cooper—Schrieffer (BCS) theory, which constitutes a satisfactory approximation in the three-dimensional case, to the calculation of the critical temperature of a superconducting junction and obtained the fantastic value $T_{cr} = 2200$ K. In other words, a system satisfying Little's model must be a superconductor over the entire temperature range of its existence.

The results of this study were subjected to a thorough and just criticism (see, for example, Refs.2–4), but it created such an enormous impression that a search was immediately begun for systems formally satisfying Little's model. The initial aim was to increase the critical temperature for superconduction: this led to the creation of new branches of the physics and chemistry of the solid state—the physics and chemistry of quasi-one-dimensional systems. Substances with a high anisotropy in physical properties were discovered primarily among the class of molecular complexes—charge-transfer complexes (CTC) and radical-ion salts (RIS). As early as 1962, the radical-anion salts of 7,7',8,8'-tetracyanoquinodimethane (TCNQ) with simple and complex compositions [Kt^+TCNQ^-, $Kt^+(TCNQ)_2^-$, and $Kt_2(TCNQ)_3^{2-}$, where Kt is the metal or organic base action], were described in a review[5]. A characteristic feature of systems of this kind is an unusual quasi-one-dimensional nature of the packing of the salt components in the crystal in which the TCNQ molecules form infinite columns of interleaved and non-interleaved types (Fig.1).[6,7]

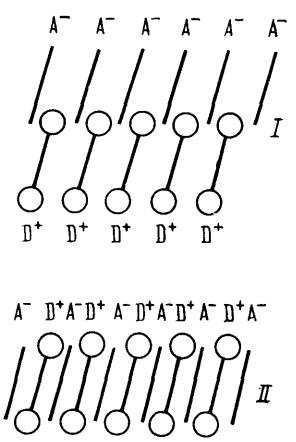


Figure 1. Types of molecular packing of CTC: II) interleaved type; I) non-interleaved type; A = acceptor; D = donor.

In 1968 Krogmann obtained planar mixed valence complexes with metal—metal bonds based on platinum cyanide (Krogmann salts)[8,9]. These salts have the composition $K_2Pt(CN)_4.X_{0.3}\cdot nH_2O$ (X = Cl or Br) and exhibit a distinct anisotropy of their

electrical, magnetic, and optical properties[10-12]. Compounds with a similar structure were obtained by Krogmann on the basis of complex platinum oxalates, for example, $Mg_{0.82}\cdot[Pt(C_2O_4)_2].5.3H_2O$ and $K_{1.6}[Pt(C_2O_4)_2].2H_2O$.[13,14] Highly conducting compounds with a quasi-one-dimensional structure, based on iridium carbonyl halides having the composition $K_n[Ir(CO)_4Cl_m]$, have been described[15]. The physical properties of the above compounds have been examined in detail in a review[16] and therefore not discussed here. Particular attention has been devoted to the properties of organic conductors, their synthesis, and purification in the review of Khidekel' and Zhilyaeva[17].

The present review surveys the results of experimental and theoretical studies on highly anisotropic molecular solids (excluding polymers) obtained after the publication of previous reviews[16,17].

II. THEORY OF LINEAR CONDUCTING SYSTEMS

Numerous studies have been made on the nature and stability of the metallic state in quasi-one-dimensional systems. It was therefore necessary to develop new methods of calculation taking into account the interaction between one-dimensional filaments, which is very significant for phase transitions in quasi-one-dimensional crystals (phase transitions are impossible in a rigorously one-dimensional crystal[4]).

In order to explain the electrical properties of charge-transfer complexes (CTC), many different models have been proposed. The most natural model is that of bilinear organic conductors in which the conductivity of the crystal is assumed to be additive to a first approximation. On the basis of this model, Phillips[18,19] explained the characteristics of the electrical properties of organic conductors by the appearance of domains with a Peierls structure. It is assumed that the sizes of the Peierls energy gaps are different for donor and acceptor columns and the lattice periods are therefore also different. The domains with a Peierls structure are formed when the difference between $E_A(T)$ and $E_D(T)$ is small. This type of structure disappears in a first order-phase transition. The Phillips model is applicable to TCNQ complexes; in particular, it explains the observed temperature dependence of the electrical conductivity $\sigma(T)$, which varies in proportion to T^{-n} $(n>1)$ when $T > T_p$. The domains alternate with metallic regions whose length is of the order of hundreds of angstroms. The charge can migrate not only along the chains but also between them—via jumps.

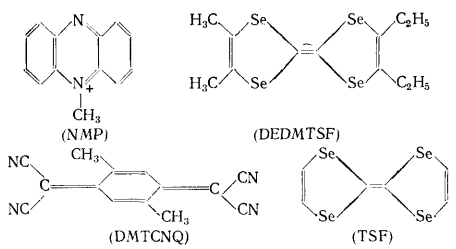
The structure of the CTC depends significantly on the Coulombic electrostatic interaction, on the elucidation of the role of which numerous studies have been carried out[20-27]. The charge transfer in the formation of the CTC leads to a considerable increase of the electrostatic energy owing to the repulsion of the charges of the neighbouring molecules in the column. This energy decreases either owing to the formation of complex salts or as a result of incomplete charge transfer. The possibility then arises of a resonance electron transfer via a relay mechanism:

$$\text{—}A^-\text{—}A^0\text{—}A^-\text{—}A^0\text{—} \rightarrow \text{—}A^0\text{—}A^-\text{—}A^0\text{—}A^-\text{—} .$$

In the tetrathiofulvalene—tetracyanoquinodimethane (TTF–TCNQ) complex there is not only incomplete charge transfer but charge density waves (CDW) are generated with a wave vector $4k_F$ ($\hbar k_F$ is the Fermi-quasi-momentum)[20]. The instability as regards the formation of the CDW is the only type of instability occurring at finite temperatures in the one-dimensional chain of a quasi-one-dimensional conductor and is due to the Coulombic electrostatic interaction and the interaction between the electrons and phonons of the three-dimensional crystal[21]. On decrease of temperature, a phase transition takes place in systems of this kind to a state with CDW, accompanied by the distortion of the lattice with a period $(4k_F)^{-1}$. In an ordered state non-linear CDW excitations constitute solitions with a gap in the excitation spectrum. Analogous collective states of a one-dimensional electron gas, which can be interpreted as isolated or bound solitons, can conduct an electric current[22,23]. The dependence of the current transmitted by solitons on temperature is of the activated type. The soliton model has been discussed in connection with the attempt to interpret the electrical conductivity peak in the TTF–TCNQ crystals[24].

The interaction of a rarefied electron gas with a highly polarised background can lead to an effective electron—electron repulsion. There is then a possibility of the Wigner "crystallisation" of the electron gas either in the form of individual electrons or in the forms of pairs[25-27]. The presence of such a generalised lattice makes it possible to interpret the optical spectra of TCNQ salts and to explain the satellite reflections on X-ray diffraction patterns[28]. The structure arising in the TTF–TCNQ complex is of the antiferroelectric type.

In systems containing components with a low symmetry there is a possibility of instability due to orientation disorder. The symmetry of planar centrosymmetric molecules can decrease as far as C_s following the introduction of one of two substituents. Examples of such compounds are provided by the complexes NMP–TCNQ, DEDMTSF–TCNQ (contain only asymmetric cations), TSF–DMTCNQ (contains only asymmetric anion), and others†.



One of the alternative possibilities in the packing of asymmetric fragments in the column is orientationally disordered packing. The influence of such disorder on the instability of the Peierls type has been examined[29]. The breakdown of translational symmetry on orientational deformation merely modulates, in contrast to shear deformation, the local energy of the electron, leaving unchanged the transition integrals. The gap in the electronic spectrum is then absent and the Peierls transition does not arise. Allowance for the interaction of the electrons of the one-dimensional chain with the rotational vibrations of the organic molecules (librons) demonstrated the possibility of the existence of states with the so-called chiral charge density waves (CCDW). A lattice instability with a wave vector $\mathbf{Q} = 4\mathbf{k}_F$ corresponds to these. The transition to the state with CCDW can account for the continuous variation of the superstructure period from a to $2a$ and then to $4a$ in the TTF–TCNQ crystals, which occurs in the range 54–38 K. The electron-libron interaction is also very significant in TSF–TCNQ and $(TTF)_7I_5$.[30]

† Notation: NMP = *N*-dimethylphenazinium ion; DEDMTSF = diethyldimethyltetraselenofulvalene; DMTCNQ = dimethyltetracyanoquinodimethane; TSF = tetraselenofulvalene.

The lattice instability of the quasi-one-dimensional crystals is due in the general case to two fundamentally different contributions-dimerisation of the Peierls type via electron–phonon interaction and spin-Peierls dimerisation due to the spin–lattice interaction. The two different contributions have been estimated[31] using the self-consistent field approximation. Intermediate values of the interelectron interaction constants for which the electronic states are still delocalised, i.e. $t \propto U$, were taken. Here t is the integral for the transition of an electron between two nearest electronic states and U is the energy of the interaction of two electrons at a single site. By virtue of the quadratic relation between the exchange integrals and the transition integrals ($J \propto t_2$), the spin–lattice interaction is more effective than the electron–lattice interaction for intermediate values of t/U and for this reason the spin-Peierls transition is more probable than the Peierls transition.

The radical-anion salt $K^+TCNQ^{-\cdot}$, which undergoes a phase transition at 396 K, formally satisfies this model. Here there is a change in the energy gap and a complex rearrangement of the one-dimensional chain takes place and is accompanied by a rearragement of the spin structure. For this reason $K^+TCNQ^{-\cdot}$ is a spin system which exhibits Peierls instability in the vicinity of Tp.[32]

Ideas about the spin-Peierls instability have been used[33] to account for two Konno anomalies in quasi-one-dimensional TCNQ salts with the wave vectors $\mathbf{k}_1 = \mathbf{b}^*\rho$ and $\mathbf{k}_2 = \mathbf{b}^*\rho/2$, where $\mathbf{b}^*$ is the inverse lattice vector along the chains and ρ is the number of conductivity electrons per molecule ($\rho < 1$). For $\rho = 1/2$, the anomaly with $\mathbf{k}_1$ is caused by the electron–phonon interaction in which pairs of molecules containing one electron are combined into diads. The anomaly with $\mathbf{k}_2$ corresponds to the Peierls transition, i.e. the transition to the antiferromagnetic state in which the electrons of neighbouring diads form singlet pairs (it is assumed that $T_1 > T_2$). The lattice period is then quadrupled.

Studies on the infrared spectra of conducting quasi-one-dimensional crystals of TCNQ salts, initiated by Kaplunov et al.[34] and Kondow and Sakata[35], revealed their fundamental difference from the spectra of other molecular crystals. A characteristic feature is the presence of a broad absorption band associated with intermolecular charge transfer along the TCNQ column, beginning on the high-frequency side in the visible part of the spectrum and embracing the low-frequency infrared region to a greater extent the higher the electrical conductivity of the complex. This band covers the region of the low-frequency intramolecular vibrations (IMV) of the TCNQ molecules. The observed spectrum is not a simple sum of the electronic and vibrational spectra and has a more complex form: anomalously broadened asymmetric lines correspond to the intramolecular vibrations of TCNQ and the polarised spectra of the single crystals contain lines corresponding to the IMV with A_g symmetry, i.e. to electrical dipolar transitions which are prohibited for an isolated molecule.

The important role of the interaction of the electron system with IMV in the interpretation of the electronic, kinetic processes in TCNQ crystals has been established in a number of theoretical studies[36–42]. Allowance for the interaction is also necessary, according to Epstein and Conwell[43], in the analysis of temperature variation of the electrical conductivity and the electron mobility in crystals of TCNQ salts. We may also note that the study of the interaction of electrons with high-frequency IMV in organic conducting crystals is of interest in connection with the problem of high-temperature super-conductivity via the phonon mechanism. The first determination of the electron–phonon interaction constants for TCNQ salts by analysing the infrared spectra of the $TEA(TCNQ)_2$ salt (TEA = tetraethylammonium) has been carried out by Belousov et al.[44]

On the basis of a phenomenological model the above workers[44] obtained a formula for the component of the dielectric constant tensor along the conducting filaments:

$$\varepsilon_{\parallel}(\omega) = \varepsilon_{\parallel}^{\infty}\left[1 + \frac{(\omega_{le}^2 - \omega_{tl}^2)}{\omega_{te}^2 - \omega^2 - ig_e\omega - \sum\limits_k \gamma_k^2/(\omega_k^2 - \omega^2 - ig_k\omega)}\right],$$

incorporating the background dielectric constant $\varepsilon_{\parallel}^{\infty}$, the longitudinal frequency ω_{le}, the intrinsic frequency ω_{tl} of a one-dimensional harmonic oscillator describing the electronic transition with a decay coefficient g_e, the frequency ω_k and the decay coefficient g_k of IMV of type k, and the interaction constant γ_k.

This formula describes effects associated with the frequency shift and the occurrence of forbidden transitions known for Fano resonance[45]. The optical conductivity $\sigma(\omega) = \omega \mathrm{Im}\varepsilon_{\parallel}(\omega)$ spectrum differs significantly from the sum of the electronic and vibrational spectra. The spectrum illustrated in Fig. 2 is a result of the interference of the electronic and vibrational states and corresponds to the antiresonance of a continuous spectrum with a set of discrete vibrational levels. For example, the ω_k vibration, located on the low-frequency slope of the electronic band is manifested by an asymmetric band (with a width much greater than g_k), beginning with a shallow minimum on the high-frequency side, at a frequency close to ω_k. The vibration

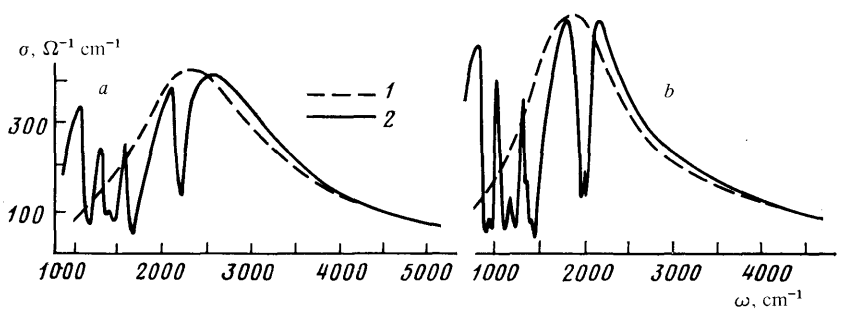


Figure 2. Spectroscopic relations for the optical conductivity of $TEA(TCNQ)_2$ crystals with E polarisation[44]: *1*) unperturbed electronic band; *2*) the same band with allowance for the interaction with intramolecular vibrations: *a*) 300 K; *b*) 100 K.

occurring in the region of the maximum of the electronic band is manifested by a "crossing-over point".

It has been shown[46] that the high dielectric constant of the salt TEA $(TCNQ)_2$ is due to the interaction of the low-frequency intramolecular TCNQ vibrations with electrons, leading to the formation of mixed electron-phonon states with a high oscillator strength.

The theoretical studies undertaken to elucidate the relation between the temperatures of the superconducting transition (T_c) and the Peierls transition (T_p) are important. It is known[47] that, to a first approximation, $T_c \cong T_p$ or the two temperatures are very similar, from which it follows that in such systems the superconductivity is fundamentally unobservable (the superconducting transition is suppressed by the dielectric transition). The two temperatures T_c and T_p increase monotonically with increase of the electron–phonon interaction constants and for low constants $T_c > T_p$, while for high constants, $T_c < T_p$.[48] This means that T_c for quasi-one-dimensional systems are hardly likely to be high, but they may nevertheless be appreciably higher than for a three-dimensional highly anisotropic metal[49]. Exciton shielding does not apparently exert a decisive influence on the electronic properties of radical-ion salts[50].

The problem of the influence of impurities in quasi-one-dimensional conductors on T_c and T_p has been studied[51,52]. For a weak electron–electron interaction, the impurities suppress the three-dimensional phase transition and increase the superconductivity fluctuation in unit chains. Marked scattering by the impurities fully suppresses the dielectric Peierls transition and, after the attainment of a certain critical concentration of impurities, the superconducting transition is also suppressed.

III. THE TETRATHIOFULVALENE–7,7,8,8-TETRACYANOQUINODIMETHANE COMPLEX

The attention of investigators has been mainly directed to a detailed study of the phase transitions in TTF–TCNQ crystals. Numerous precise measurements of the physical properties over a wide temperature range have now been carried out. The resistance R along conducting columns has been measured to within 10^{-5}. A sharp negative discrepancy at 53 K, associated with a second-order transition, has been observed in the relation between dR/dT and T.[53] The temperature dependence of the electrical conductivity in the range 20–300 K and at pressures up to 6×10^8 Pa exhibits two anomalies[54]. The temperature of the first (the metal–dielectric transition) (54 K and $p = 0$) increases with increasing pressure, while that of the second (38 K and $p = 0$) decreases slowly. Since the width of the conductivity band in the TTF–TCNQ complex increases with pressure in the experimental range of the latter, these results are difficult to interpret within the framework of the existing theory of the Peierls transition. The transitions have been interpreted[55] as independent transitions in the donor and acceptor columns, namely the transition at 54 K corresponds to ordering in the TCNQ chains while that at 38 K is associated with further ordering in the TTF chains, which leads to the appearance of a gap in the TTF column. Only one transition, at 29 K, is observed in TSF–TCNQ crystals, which can be accounted for by an intense interchain interaction.

The ability of the TTF–TCNQ and TSF–TCNQ complexes to form solid solutions makes it possible to obtain TTF_xTSF_{1-x}·TCNQ single crystals ($0 \leq x \leq 1$).[56–58]. Studies on the electrophysical properties of such crystals showed that the conductivity of the TTF–TCNQ crystal is determined by TCNQ chains in the range 300–58 K and by TTF chains in the range 58–38 K. The conductivities of the donor and acceptor columns in the TSF–TCNQ crystals are of the same order of magnitude. It therefore appears likely that both donor and acceptor columns are responsible for the transition at 38 K in TTF–TCNQ. The simple phase transition in TSF–TCNQ splits into two components after the addition of small amounts of TTF–TCNQ (<2%). The temperature of the high-temperature transition increases rapidly with increasing TTF concentration, while that of the low-temperature transition diminishes slowly, but the region of the anomaly in the resistance associated with this transition is markedly broadened.

Measurements of the velocity of sound in the range 0–300 K established[59,60] that Young's modulus is anistotropic ($E_a > E_b$, where b is the maximum conductivity axis), increases with decrease of temperature, and diminishes by several per cent in the vicinity of the transition point (54 K), the decay of sound at this temperature passing through a maximum. The increase of the velocity of sound by 1.5% at $T < 52$ K is due to the freezing of the conductivity electrons. A singularity is observed in the vicinity of T_p in the relation between the change in the magnetic susceptibility $d\chi/dT$ and T: $d\chi/dT \propto (T - T_p)^{1/3}$ and $\chi \propto \Delta^2$, where Δ is the width of the dielectric gap. There are no singularities on the $\chi(T)$ and $(d\chi/dT)(T)$ curves near the second transition[61], but they are manifested clearly on the $\chi(T)$ curve after the isolation of the contribution by the background (Fig. 3).[62]

Precise measurements of the heat capacity of the TTF–TCNQ crystals revealed four phase transitions, at 52.6, 48, 46, and 37 K,[63] while precise measurements of Young's modulus in the range 54–38 K led to the differentiation of five phase transitions[64]. These transitions can be regarded as martensite transformations in which the effects of the elastic interaction and of the ordering of microdomains, leading to one- and three-dimensional distortions of the lattice, play a significant role. The anomaly at 46 K is associated with a phase transition in the surface region, corresponding to the transition at 49 K in a massive specimen.

Measurements of neutron scattering in the range 38–54 K revealed the existence at $T < 38$ K of a three-dimensional structure with modulation of long-range order along the a and b axes in the initial monoclinic lattice with periods of $4a$ and $3.4b$.[65] The magnetoresistance of the TTF–TCNQ crystals $\Delta\rho/\rho = [\rho(50\text{ K}) - \rho(0)]/\rho(0)$ is smaller by 0.1% in the temperature range $T > 54$ K,[66] while at $T = 52.8$ K there is a magnetroresistance peak of 1.4%. The temperature T_p decreases in a magnetic field in accordance with the law

$$\Delta T \propto (\mu_B H)^3 (2k_F)^2 T_p$$

The results of Cooper et al.,[67] who investigated the influence of the isotope substitutions $^2H \rightarrow {}^1H$ and $^{15}N \rightarrow {}^{14}N$ on the transitions at 52.5 K (T_1) and 37.7 K (T_2), confirmed the view that the transitons in the TTF and TCNQ columns are independent. When both chains are deuterated, T_1 increases by 0.75 K, while the substitution of ^{14}N results in an increase by 0.6 K. When only TTF is deuterated, T_1 remains unchanged, but T_2 is altered. On the other hand, when only TCNQ is deuterated, T_1 increases by 0.7 K, while T_2 remains unchanged. This result can be explained by the fact that all molecular vibrations contribute to the Peierls instabilities; their relative contributions are determined by the binding constants. In TCNQ chains the instability is determined mainly by the intramolecular vibrations[68].

Several theoretical models have been proposed to account for the phase transitions in the range 38–54 K.[69–74]. The transitions at 54, 49, and 38 K can be accounted for on the basis of the Ginzburg–Landau theory. In contrast to the generally accepted interpretation, it has been claimed[73] that

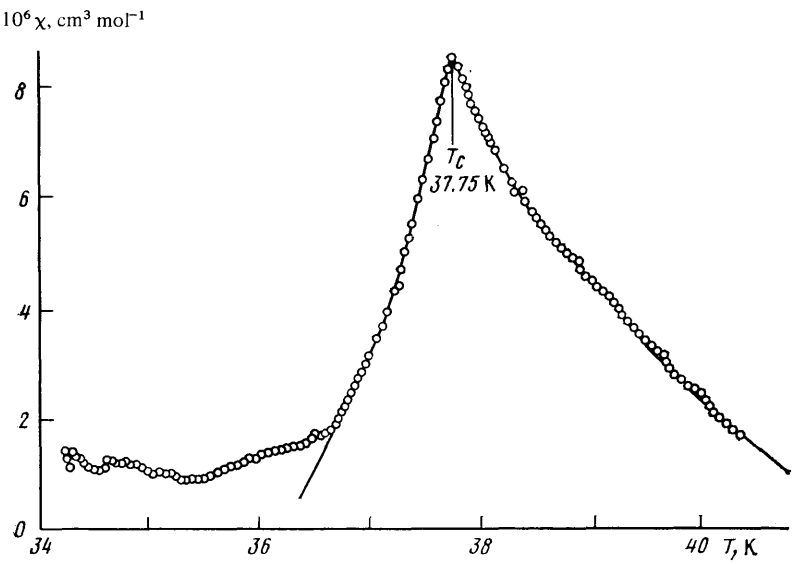


Figure 3. The anomaly in the magnetic susceptibility of the complex TTF–TCNQ near 38 K after the isolation of the background, giving rise to an exponential $\lambda(T)$ relation[62].

the transition at 54 K is associated with ordering in both filaments and not only in the TCNQ column. Experiments on X-ray scattering[72] made it possible to relate the transition at 54 K to the condensation of the anomaly with the wave vector $2\mathbf{k}_F$ in the form of the $2a \times 3.4b \times c$ superstructure, while the transition at 49 K can be related to the condensation of both longitudinal anomalies with the vectors $2\mathbf{k}_F$ and $4\mathbf{k}_F$.

In order to explain the microanomalies of Young's modulus in the range 38–52 K, a model based on the idea of the domain structure of the metallic and dielectric phases has been proposed[70]: it is believed that the column consists of conducting and non-conducting sections separated by domain walls consisting of a separate phase. The transition at 47 K corresponds to the formation of tetrads made up of metallic domains, while the transition at 38 K corresponds to their ordering. The transition at 34 K corresponds to the disappearance of metal–dielectric microdomain transitions from the TCNQ columns[70,71]. The transitions at 49–54 K have also been interpreted using the concept of phasons—excitations of the ground state with CDW which infringe the symmetry as a consequence of the phase shift of the CDW of the neighbouring chains[69]. The transition at 49 K corresponds to the instability of the phason mode. In this model there is a linear (in terms of the phason amplitude) interaction with a deformation of the crystal and the transition can therefore be suppressed by the application of an appropriate pressure. Thus, despite the abundance of experimental data, the theoretical interpretation of the results is not yet clear mainly due to the lack of a general theory of quasi-one-dimensional systems.

A series of detailed experimental studies have been made on the influence of the purity and perfection of TTF–TCNQ crystals on their electrophysical properties as well as the influence of the methods of measurement. One of the possible ways of taking into account the influence of the direction of the crystals is statistical analysis of the results of different workers. Such analysis, based on a survey of 600 measurements in 18 world laboratories[75], shows that the hypothesis of superconducting fluctuations is superfluous. The temperature T_P is in the range 54–58 K;[76] the scatter of the values is determined mainly by the degree of perfection of the single crystals and to a lesser extent by the concentration of the impurities.

This has been shown for TTF–TCNQ crystals with impurity concentration not exceeding 10^{-6}.[77,78] As a consequence of the low value of the disproportionation energy of the $TCNQ^-$ and TTF^+ radical-ions, the TTF–TCNQ crystals possess an internal source of contamination and, according to Haddon's data[79], the concentration of the impurities formed on disproportionation via the mechanisms

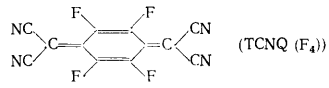
$$2TCNQ^{\bullet-} \rightarrow TCNQ^0 + TCNQ^{2-},$$
$$2TTF^{\bullet+} \rightarrow TTF^0 + TTF^{2+},$$

can reach 12%. Crystals grown from the gas phase are not free from such contamination either. This follows from the scatter of the values of σ_b (at 300 K) for such crystals, which are in the range $(2\text{–}6.7) \times 10^4\ \Omega^{-1}\ m^{-1}$.[80] A very great change in σ in the region of 58 K has not been observed either for large TTF–TCNQ crystals whose dimensions were $7 \times 0.5 \times 0.24$ mm and $30 \times 6 \times 0.7$ mm.[81] The concept of the anisotropy of σ arises from measurements of its principal values for a series of crystals: $\sigma_b = (4.40 \pm 0.15) \times 10^4$, $\sigma_a = (1.30 \pm 0.05) \times 10^2$, and $\sigma_c = (12.6 \pm 30.0) \times 10^2\ \Omega^{-1} m^{-1}$.[82] The scatter of the values of σ_c is due to the small thickness of the crystals in the direction of the c axis and the possible diffusion of the current-conducting silver paste through the crystal.

The magnitude of the transferred charge Δq in TTF–TCNQ crystals is important for the construction of a theoretical model for the latter. It has been determined by various methods and the scatter of its values proved to be small. Direct numerical integration in terms of X-ray structure factors yields $\Delta q = (8.55 \pm 0.95) \times 10^{-20}$ C.[83] Experiments on Raman scattering by TTF, TTF–TCNQ, and $(TTF)_7I_5$ crystals[84] in the temperature range 4–77 K yielded $\Delta q = 7.92 \times 10^{-20}$ C.[85] Two peaks of the $N1s$ levels have been observed

in the X-ray photoemission spectra, which corresponds to two TCNQ charge states (neutral and singly ionised)[86]. The ratio of the intensities of these peaks, proportional to Δq, yields the estimate $\Delta q \cong (8.87-10.61) \times 10^{-20}$ C.

Silverman[87] suggested that Δq for CTC is always smaller than unity, while for TTF-TCNQ it amounts to 9.35×10^{-20} C. All the results quoted above confirm the conclusion[88] that the optimum value of Δq, necessary for the preparation of highly conducting CTC, is $(9.50-12.67) \times 10^{-20}$ C per molecule. This is associated with two opposed factors: an increase of q entails an increase of the concentration of the conductivity electrons (and hence also of σ) and at the same time an increase of the Coulombic repulsion of the electrons, leading in the limit to the splitting of the conductivity band and the formation of localised electronic states. In fact, the value of Δq estimated by X-ray electronic spectroscopy for the TTF-TCNQ complex



(TCNQ (F_4))

with a low conductivity is $(15.04 \pm 3.17) \times 10^{-20}$ C.[89] A high value of Δq is obtained as a result of the high electron affinity (higher by 0.4 eV than that of TCNQ).[90] TCNQ(F_4) can therefore be used to obtain highly conducting CTC employing weaker donors.

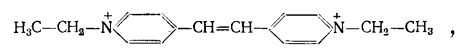
Complexes of TTF with TCNQ having a different stoichiometry are also known: $(TTF)_3(TCNQ)_2$ and $(TTF)_2TCNQ$.[91] These complexes are obtained by the low-temperature exchange method.

IV. CHARGE-TRANSFER COMPLEXES AND RADICAL-ION SALTS BASED ON 7,7,8,8-TETRACYANOQUINODIMETHANE

Simple radical-anion salts based on TCNQ have attracted the interest of both experimenters and theoreticians in connection with the fact that they exhibit two types of instability of the metallic state: the Mott and Peierls instabilities. In both of these salts a structural Peierls transition takes place at certain temperatures with retention of the Mott gap. Such a transition has been investigated[92] by X-ray diffraction for the salt Na^+TCNQ^-. In the low-temperature phase ($T < 353$ K) the distances in the $TCNQ^-$ column alternate: 3.212×10^{-10} and 3.429×10^{-10} m, while in the high-temperature phase all the distances are equalised: 3.385×10^{-10} m. The analogous transition at 396 K in K^+TCNQ^- crystals[93] is accompanied simultaneously by a rearrangement of the spin structure and K^+TCNQ^- is therefore a system which exhibits spin-Peierls instability in the vicinity of TP. According to structural and magnetic data[94], the spin-Peierls instability is also characteristic of the violet ($TP = 301$ K) and bluish-violet ($TP = 215$ K) NH_4TCNQ^- phases.

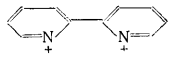
According to electrophysical measurements, heating results in phase transitions in TCNQ salts not only with alkali metals (Li, Na, and K) but also with transition metals (Mn, Fe, Co, Ni, Cu, and Zn).[95] The plot of $\lg \rho$ against $1/T$ in the range 300-500 K consists of two linear sections and of a transition region between them, the latter corresponding to a gradual accumulation of the high-temperature phase within the limits of the low-temperature phase, i.e. the transition is diffuse. In alkali metal salts of TCNQ these transitions have also been observed by infrared spectroscopy[96] from the sharp increase of the intensities of the lines corresponding to the vibrations of TCNQ molecules with A_g symmetry. The Coulombic interaction in these salts makes the main contribution to the dielectric gap, since at TP the latter decreases insignificantly.

The report[97] of the preparation of the radical-ion salt $(DEPE)^{2+}(TCNQ)_4^{2-}$, where DEPE = bisdiethylpyridiniaethylene

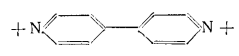


has aroused much interest among investigators. In this salt the metallic state persists up to ~0.03 K. The above communication led to a flood of publications[98-104] devoted to studies on this and similar radical-ion salts. Values of σ_{300} in the range $(1.5-22) \times 10^4\ \Omega^{-1}\ m^{-1}$ have been quoted in a number of studies[98,105,106] for the above radical-ion salt; $\sigma_{0.03}/\sigma_{300} \cong 3.7$. The thermo-e.m.f. is 35×10^{-6} V K^{-1} and is independent of temperature. However, according to Somoano et al.[99], σ_{300} of the monoclinic phase is $\sim 5 \times 10^3\ \Omega^{-1}\ m^{-1}$ and the $\sigma(T)$ relation is of the semiconducting type with an activation energy $E_a = 0.10 \times 10^{-19}$ J; the thermo-e.m.f. is saturated at high temperatures, reaching 6×10^{-5} V K^{-1}, which corresponds to a quarter-filled conductivity band. The erroneous nature of the conclusions reached in several studies[97,98,105,106] may be associated with the employment of thin $DEPE(TCNQ)_4$ single crystals, which might have resulted in the short-circuiting of the contacts owing to the diffusion of the current-conducting paste. Indeed, a semiconducting relation with $E_a = (0.32-0.48) \times 10^{-19}$ J has been obtained for a series of similar TCNQ salts[98-104], which were isolated in the form of larger crystals.

Interesting data concerning the influence of the symmetry of the cation on the electrophysical properties of the radical-ion TCNQ salts have been obtained[107]. The properties of the TCNQ radical-ion salts with symmetrical (4,4'-bipy) and asymmetric (2,2'-bipy) cations



(2,2'-bipy)



(4,4'-bipy)

are markedly different. The salt with the symmetrical cation is a semiconductor while that with the asymmetric cation is metal-like, in which the metal–dielectric transition occurs on cooling. The studies by Mihaly and coworkers[108,109] of the influence of the dipole moments of the donors are related to the above investigations. If the dipole moments are small, there is a possibility of a metallic state in which these moments are oriented at random. Scattering by the inhomogeneities of the electric field suppresses the dielectric transition and the salts behave as disordered metals. For large dipole moments, there is a possibility of the occurrence of an ordered charge state in which the salts behave as narrow-band conductors with a low conductivity.

The electrophysical properties of the TCNQ salt depends significantly also on the method of preparation (the specimens contain different amounts of $TCNQ^{2-}$ impurity ions). For example, a change in the concentration of the $TCNQ^{2-}$ ions in the salt $Qn(TCNQ)_2$(Qn = quinolinium) alters E_a from 0.37 to 0.60×10^{-19} J, while σ is reduced by a factor of 10.[110] In addition, in the course of the preparation of the TCNQ salts, the molecules of many solvents can be incorporated in the crystal lattice of the complex; this usually decreases the resistance[111]. The influence of the solvent is manifested particularly effectively in the complex $(NMeQn)(TCNQ)_2$.[112, 113] A phase transition, accompanied by a sharp decrease of σ in the high-temperature phase occurs in this complex at 390 K. The transition is due to the decrease of the content of acetonitrile in which the complex was obtained. Its evaporation increases the structural disorder in the conducting

phase. The acetonitrile molecules act as a shield preventing the interaction of neighbouring chains and stabilise the thermodynamically unstable phase.

An unusual metal–dielectric phase transition occurs on heating crystals of the salt DECA $(TCNQ)_2$ (DECA = diethylcyclohexylammonium[114]). It is an irreversible first-order transition in which the initial column, consisting of TCNQ tetrads, is converted into one consisting of diads in the high-temperature phase. Sharp anomalies are observed on curves for the temperature variation of χ and the specific heat $\rho(T)$ (Fig. 4). The temperature of the transition depends greatly on the pressure ($dp/dT \cong 16 \times 10^4$ kg m^{-2} K^{-1}).

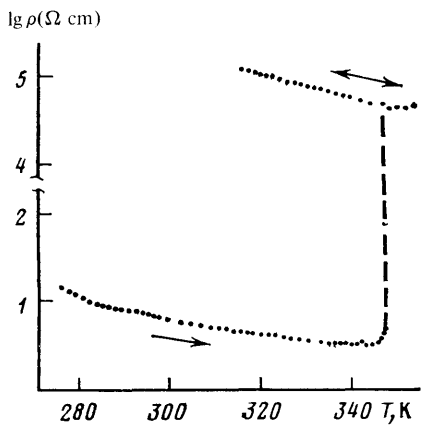


Figure 4. Temperature variation of the resistivity of DECA$(TCNQ)_2$ crystals[114].

When the salt $(NMe_3H)TCNQ$ was oxidised with iodine[115], a one-dimensional complex with a one-third filled band, having the composition $(NMe_3H)^+(I_3)^-_{1/3}(TCNQ)^{(2/3)-}$, was isolated. The anistropy of the electrical conductivity, measured by Montgomery's method, is ~400 and the conductivity $\sigma_{300} = 2000\ \Omega^{-1}\ m^{-1}$ increases up to 240 K, decreasing sharply at 160 K. The EPR line width decreases monotonically up to 160 K, after which it increases sharply. This transition is reversible and, according to the data of Delhaes et al.[116], is a Peierls transition.

Complexes formed by derivatives of dipyranylidene and its dithio-analogue, isoelectric with TTF, are of interest[117,118]. Such donors have low ionisation potentials and high polarisability. In particular, tetraphenyldiphyranylidene



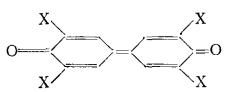
and tetraphenyldithiodipyranylidene form complexes with TCNQ; the conductivity of the first complex $\sigma_{300} \cong (2.4–4.0) \times 10^3\ \Omega^{-1}\ m^{-1}$ and decreases with decrease of temperature in accordance with an activation law ($E_a = 6.41 \times 10^{-21}$ J); the conductivity of the second complex $\sigma_{300} \cong (2.5–3.0) \times 10^4\ \Omega^{-1}\ m^{-1}$ and increases with decrease of temperature up to 145 K; below this temperature, the dielectric phase is stable. A reversible phase transition, in which σ decreases by two orders of magnitude, has also been observed in the tetraphenyldipyranylidene complex.

V. ORGANIC CONDUCTORS BASED ON CHARGE-TRANSFER COMPLEXES

Highly conducting compounds based on CTC were isolated as early as 1965 [119] using tetrathiotetracene (TTT) as the donor. *o*-Chloranil (*o*-CA), *o*-bromanil (*o*-BA), and tetracyanoethylene (TCNE) form complexes with the compositions $(TTT)_3$(*o*-CA), $(TTT)_3$(*o*-BA), and $(TTT)_3(TCNE)_2$. The resistances of the powdered specimens vary in accordance with an activation law ($E_a \cong 1.6 \times 10^{-20}$ J) and have the following values at 300 K:

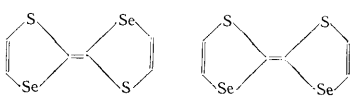
Acceptor	*o*-CA	*o*-BA	TCNE
$10^2\rho_{300}$, Ωm	2.4	6–8	15

Tetrahalogenodiphenoquinones have high electron affinities:

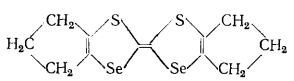


In particular 4.49×10^{-19} J, which is identical with the electron affinity of TCNQ, has been obtained for TCDQ and TBDQ.[90] The quinonoid structures of these complexes suggest a high polarisability. A series of TCDQ and TBDQ radical-ion salts have been described[120,121]. Salts containing cations, such as that of *p*-phenylenediamine (a Wurster radical-cation), ferrocenium, and cobaltocenium (0.2–0.8 Ωm, pelletted specimens) have low resistivities. Highly conducting complexes $TTT(TCDQ)_2$ and $TTT(TBDQ)_2$ are also formed by tetrathiotetracene[122] ($\sigma_{300} \cong 1.7$ and 8 Ω^{-1} m^{-1} respectively). It follows from infrared spectra that these complexes are radical-ion salts. Unfortunately, as a consequence of the extremely limited solubility of the RIS based on TCDQ and TBDQ, it is virtually impossible to isolate the salts in the form of single crystals.

Complexes of substituted derivatives and analogues of TTF with TCNQ and its derivatives have now been investigated in detail. As a rule, the weak asymmetry of the donor or acceptor stabilises the metallic phase of the complex, in which the latter behaves as a disordered metal. For example, mixed *cis–trans*-diselenodithiofulvalene (DSDTF)

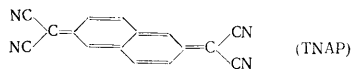


forms with TCNQ a complex having $\sigma_{300} = (7 \pm 3) \times 10^4\ \Omega^{-1}\ m^{-1}$, [123] which behaves as a disordered metal. Its dicyclopentano-derivative



(HMDSDTF)

forms with TCNQ and TNAP (11,11',12,12'-tetracyanonaphtho-2,6-quinodimethane)



(TNAP)

highly conducting RIS with the 1:1 composition ($\sigma_{300} \cong 10^4\ \Omega^{-1}\ m^{-1}$). [124] The complex of TMTTF (tetramethyltetrathiofulvalene) with 2,5-dimethyl-TCNQ has the conductivity $\sigma_{300} \cong 5 \times 10^4\ \Omega^{-1}\ m^{-1}$ with a sharp maximum at 50 K ($\sigma_{50}/\sigma_{300} = 10$) followed by the transition to the dielectric phase[125]. The addition of MTCNQ (methyl-TCNQ) to the complex TSF–TCNQ gives rise to the mixed complex $TSF(TCNQ)_{1-x}$-$(MTCNQ)_x$,

whereupon the peak in the $\sigma(T)$ relation shifts towards higher temperatures (from 40 to 75 K) and the gap in the electronic excitation spectrum in the region below the transition temperature diminishes so much that $\sigma_{4.2}$ for the mixed complex exceeds $\sigma_{4.2}$ for the initial complex by a factor of 10^4 (Fig.5). The complexes of TTF with 2,5-diethyl-TCNQ and 2,5-dimethyl-TCNQ are also disordered conductors, but the Peierls transition occurs at higher temperatures ($Tp \cong 180$–210 K) and the increase in σ amounts to only 50 and 20% respectively[125] (Fig.6). According to thermo-e.m.f. measurements the isostructural series of the CTC of TCNQ with TTF and *cis-trans*-DSDTF exhibits the properties of semiconductors at high temperatures, while in the range 40–60 K there is a transition to the dielectric phase[127]. For example, the conductivity maximum in DSDTF–TCNQ crystals is observed at 60 K.[128] The complexes# of OMTTF, OMDSDTF, DBTTF, and DBDSDTF with TCNQ and TNAP are dielectrics[124,129]. Possibly the reason for this is the appreciable difference from the planar structure of the dicyclohexano-derivatives, on the one hand, and the high ionisation potentials of the dibenzo-derivatives, on the other.

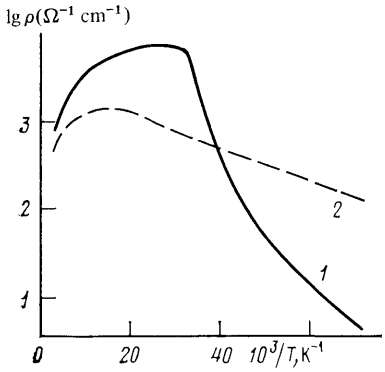
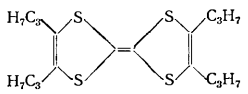


Figure 5. The electrical conductivity of TSF–TCNQ (curve *1*) and $TSF(TCNQ)_x(MTCNQ)_{1-x}$ (curve *2*) crystals[126].

Similarly the complex of the tetrapropyl derivative of TTF with TCNQ



(TPTTF)

is a dielectric having a structure of the interleaved type[130], while the magnetic and dynamic properties of the complex TMTTF–TCNQ (TMTTF = tetramethyl-TTF) are similar to those of TTF–TCNQ.[131] Apparently the main reason for this is the presence of a bulky substituent and hence an insufficiently effective overlap in the column consisting of TPTTF molecules alone.

#Notation: OMTTF = octamethylene-TTF, OMDSDTF = octamethylene-DSDTF, DBTTF = dibenzo-TTF, DBDSDTF = dibenzo-DSDTF, TNAP = tetracyanonaphthoquinodimethane, and HMTTF = hexamethylene-TTF.

However, the complex HMTTF–TCNQ (it contains a non-planar cation) exhibits a metallic type of conductivity up to ~75 K, after which it is converted into the dielectric phase[132]. The two sharp transitions at 49 ± 1 and 43 ± 1 K have been related to the rearrangement of the HMTTF and TCNQ columns respectively. Furthermore, the complex HMTSF–TCNQ (where HMTSF = hexamethyltetraselenofulvalene) retains the metallic type of conductivity up to 0.06 K. Apparently the deviations from the planar structure of these donors are not sufficiently significant to prevent an effective overlap of the donor orbitals in the column. The interaction between the HMTSF and TCNQ columns, manifested by short-circuited intermolecular contacts, has also been observed in the complex HMTSF–TCNQ.[133] In all probability this effect stabilises the metallic phase. Measurements of the anisotropy of the conductivity of organic semiconductors[134] (see Table) have shown, however, that the HMTSF–TCNQ crystal is far from being isotropic. To some extent, it can be regarded as an anisotropic quasi-two-dimensional conductor formed by layers oriented along the *a* and *b* axes.

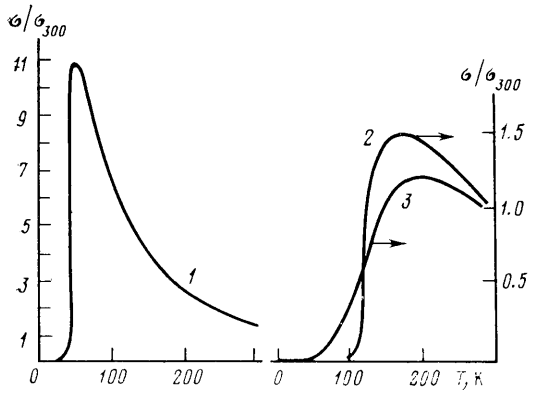


Figure 6. Temperature variation of the electrical conductivity of CTC containing low-symmetry acceptors: *1*) TMTSF–DMTCNQ; *2*) TTF-DETCNQ: *3*) TTF–MTCNQ.[125]

The anisotropy of the conductivity of organic conductors at 300 K.

Conductor	σ_b/σ_a	σ_b/σ_c	$10^4\sigma_{b_{300}}$ Ω^{-1} m^{-1}
TTF—TCNQ	300—500	120	4±1
TSF—TCNQ	150—300	130—280	8±1
HMTSF—TCNQ	30	450	18±2

The high anisotropy of the conductivity of the complexes TMTSF–TCNQ, TMTTF–TCNQ, and DEDMTSF–TCNQ has been observed by Andersen[135]. In interpreting these results, one may conclude that, in compounds containing sulphur, the current flows via both donor and acceptor columns, while in compounds containing selenium it flows only via acceptor columns. Two phases—conducting and dielectric—are known for the complex TMTSF–TCNQ.[136]

In general, polymorphism is a very common phenomenon for CTC. Polymorphism is possible for identical compositions and can be due to different contents of the solvent. Polymorphism of type P_1 is known for NMP–TCNQ, Et_2TCl. $.(TCNQ)_2$ (Et_2TCl = 3,3′-diethylthiazolinecarbocyaninium ion), RbTCNQ, TMPD–CA, and K^+CA^-.[137] The two forms can crystallise simultaneously; they can be frequently distinguished even visually and in other cases a difference is observed when the optical or electrophysical properties are investigated.

The incorporation of solvent molecules in the CTC lattice (P_2 polymorphism, i.e. polymorphism of the second kind) can alter markedly the physical property of the complex. The complex $TTT(TCNQ)_2$ incorporates acetonitrile, chlorobenzene, or nitrobenzene molecules, which leads to a highly disordered structure. The complex benzidine–TCNQ incorporates methylene chloride or benzene.

Cooling of K^+CA^- crystals, containing a one-dimensional chain of radical-ions CA^-, leads to a phase transition, which is clearly manifested on the $\chi(T)$ curve (Fig.7).[138] The susceptibility of the low-temperature phase is described equally satisfactorily by the singlet–triplet excitation model and the Ising model. The hydrated form of the salt is diamagnetic in the range 70–300 K, which is associated with the stabilisation of the singlet ground state (in the hydrated form the CA^- chain consists of singlet dimers).

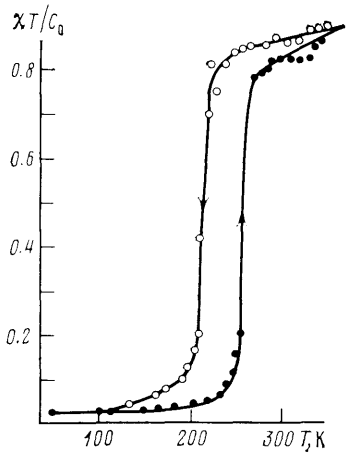
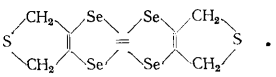


Figure 7. Temperature variation of the magnetic susceptibility of K^+CA^- crystals; $\chi T/C_0$ = dimensionless parameter; C_0 = Curie constant.

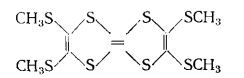
An idea about the influence of the nature of the donor on the electrophysical properties of the CTC is provided by the temperature Tp determined[139] from measurements of the dielectric susceptibility:

CTC	TTF–TCNQ	DSDTS–TCNQ	TSF–TCNQ	$TTF_{0.97}TSF_{0.03}$TCNQ	TMTTF–TCNQ
T_P, K	53	50	29	50	40

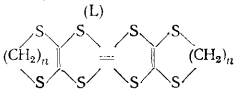
The metallic phase becomes more stable both on replacement of sulphur by selenium and after the introduction of a substituent with a small bulk. In both cases the intermolecular contacts between the donor and acceptor columns are improved. A series of donors, which are analogues of TTF but are superior to the latter as regards their electron-donating capacity, have been synthesised; for example, di-2,5-dihydrothieno-1,4,5,8-tetraselenofulvalene is structurally similar to HMTSF:[140]



It forms a 1:1 complex with TCNQ, whose conductivity $\sigma_{300} = 6 \times 10^4\ \Omega^{-1}\ m^{-1}$. A series of TTF derivatives with a still higher sulphur content, namely alkylthioderivatives, have been obtained:

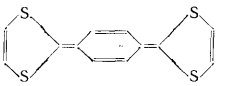


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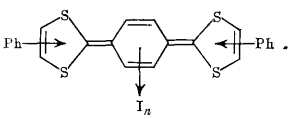
n=2 (Q); n=3 (R).

These donors form with TCNQ CTC having the composition L(Q,R)TCNQ in the form of black crystals. The conductivities σ_{300} of the complexes Q–TCNQ and R–TCNQ are higher than that of TTF–TCNQ, while σ_{300} for L–TCNQ is lower[141]. Finally the derivative of a superdonor, namely tetrathioquinodimethane



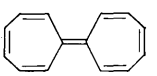
(TTQ)

was isolated in the form of diphenyl-TTQ iodide:



This iodide exists in the form of an equilibrium mixture of the RIS and the CTC.[142] The neutral TTQ has been obtained only in the form of a red solution in benzene which is extremely unstable as regards oxidation.

The study of the electronic absorption spectra of solutions of heptafulvalene



and TCNQ showed that the application of this donor (isoelectronic with TTF) is promising for the synthesis on its basis of CTC and RIS.[143] Unfortunately the complex was not isolated from solution.

Thus the only CTC retaining metallic properties at helium temperatures is the complex HMTSF–TCNQ)conductivity of the metallic type is retained by this complex at pressures $p > 2.5 \times 10^8$ Pa and temperatures up to 2×10^{-2} K).[144] At low temperatures it exhibits a high and anisotropic magnetoresistance and a high mobility of carriers (~$4 \times 10^8\ m^2\ V^{-1}\ s^{-1}$ for electrons and $1.2 \times 10^8\ m^2\ V^{-1}\ s^{-1}$ for holes). The disappearance of magnetoresistance at temperatures above 80 K indicates the one-dimensional nature of the system at these temperatures. The magnetic susceptibility increases with temperature. A considerable Hall e.m.f. was observed for the first time for quasi-one-dimensional conductors in the complex HMTSF–TCNQ.[145,146] The possibility of this effect in quasi-one-dimensional conductors was predicted by Lyo[147]. In the two-band model of the CTC the Hall mobility is caused either by a jump mechanism (when the bands do not overlap) or by resonance tunnelling (overlapping or coinciding bands). The Hall constant R_H for HMTSF–TCNQ crystals is positive at

high temperatures, increases on cooling down to 50 K, and then changes sign at 32 K, which implies an increase of the contribution of electrons to conductivity compared with holes on cooling.

The Hall effect has also been observed in TTF–TCNQ crystals by means of d.c. measurements[148] and by the ultrahigh frequency method[149]. At room temperature the value of R_H measured using a direct current is $-(4.2 \pm 0.6) \times 10^{-5}$ V Wb^{-1} m^{-1}, which agrees with the conclusion[55] that the acceptor columns make a dominant contribution to the electrical conductivity of the complex TTF–TCNQ.

VI. ORGANIC CONDUCTORS BASED ON RADICAL-CATION SALTS

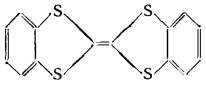
Conductors based on radical-cation salts with simple, *mainly inorganic anions possess hole type conductivity*. At the present time such conductors have been obtained from derivatives and analogues of TTF, TTT (tetrathiotetracene), and TST (tetraselenotetracene). Their composition can be expressed by the formula DY_n (where D = TTF, TTT, or TST and Y is an inorganic anion), n being as a rule non-integral.

The methods of synthesis of the radical-cation salts have been discussed in a review[17]. The halides are frequently obtained by the direct oxidation of solutions of donors by solutions of the corresponding halogens. The donor : halogen ratio, which can be varied within wide limits, determines the composition of the salts.

Direct oxidation of TTF with iodine and bromine yields salts having the composition $TTF(I)_{0.71}$ and $TTF(Br)_{0.71}$.[150, 151] The conductivity of the bromide is $(300–350) \times 10^2$ Ω^{-1} m^{-1}, changes little in the range 180–300 K, and rapidly decreases below 180 K with an activation energy of 0.13×10^{-19} J. The electrical conductivity of the iodide crystals is $\sigma_{293} = (1.0–4.5) \times 10^4$ Ω^{-1} m^{-1} and diminishes sharply at 240 K, exhibiting a considerable hysteresis. In the region of the transition there are anomalies both in the thermo-e.m.f. and in the intensity of the EPR lines. All these features are associated with a strong interaction of the one-dimensional chains in the salt crystals and also with the change in the interaction of iodine with the TTF columns in the region of the metal–dielectric transition[152].

The thiocyanates of those donors whose composition depends on the initial reactant ratio and the structure of the donors have been obtained by the direct oxidation of TTF and TMTTF by solutions of dithiocyanogen $(SCN)_2$: TTF forms the salts $TTF(CNS)_{0.5}$ and TTF(SCN), while TMTTF gives rise to salts with the compositions TMTTF.$(SCN)_{0.5}$ and TMTTF$(SCN)_2$ (the latter is a dielectric[153]). When the donor : halogen ratio was varied in the range from 1 : 0.5 to 1 : 8, a series of TMTTF salts with the following compositions were obtained: $(TMTTF)I_n$ (n = 0.5, 1.3, 2.6, and 3.7) and $(TMTTF)Br_n$ (n = 0.5, 0.8, and 6.0).[154]

A series of radical-ion salts have been obtained by oxidising TTF with copper(II) chloride and the composition of these salts depends on the nature of the solvent. The purple complex $(TTF)_3(CuCl_2)_5$, containing TTF^{+} and TTF^{2+}, was isolated from ethanol[155]. After recrystallising from acetonitrile, a black acicular salt $(TTF)_2CuCl_4$ is obtained, while direct oxidation in acetonitrile yields the yellow product $TTF^{2+}(CuCl_4)^{2-}$.[155] A series of organic conductors based on dibenzotetrathiofulvalene



(DBTTF)

have been isolated on oxidation of the latter with metal salts. In particular, the salts $D(SnCl_6)_{0.375}$, $D_4Ti_2Cl_9$, $D_8Pt_2Cl_9$, D_2PtCl_5, $D_7Pt_2Br_9$, $DPtBr_5$, D_2FeCl_4, $DFeCl_4$, $D(PtCl_6)_{0.375}$, $D(SnCl_6)_{0.375}$, and $D_{2.5}FeCl_4$ (here D = DBTTF) were obtained[156–159]. The salts $D(MCl_6)_{0.375}$ (M = Pt or Sn) and $D_{2.5}FeCl_4$ are conductors, passing to the state of a Peierls dielectric at 180–200 K. They contain DBTTF with a formal degree of oxidation of 0.75–0.8, which is most favourable for the occurrence of the metallic state[88].

The method of synthesis of radical-cation salts by an exchange raction is effective in many instances. For example, the thio- and seleno-cyanates of TTF having the compositions $(TTF)_{11}Y_6$ (Y = SCN or SeCN)[160,161] and $(TTF)_7I_5$ have been isolated. They are all isomorphous, but the iodide is a semiconductor, while the thio- and seleno-cyanates are conductors up to 220 K. Somoano et al.[162] quoted a different composition of the thio- and seleno-cyanates, namely $(TTF)_{12}Y_7$. The thermo-e.m.f. of these salts is positive and decreases linearly as the temperature is reduced, which confirms the metallic type of their conductivity and implies that the current carriers are holes.

One of the effective methods of synthesis of radical-cation salts involves oxidation with hydrogen peroxide in the presence of the corresponding acid. The oxidation of DBTTF in the presence of HBF_4 in benzonitrile yields the salt $DBTTF(BF_4)_{0.80}$.[163] The conductivity of compressed salt specimens ($\sigma_{300} \cong 80$ Ω^{-1} m^{-1}) changes little on cooling to 180 K, after which there is a sharp transition to the dielectric phase. The substance then remains in the paramagnetic phase and for this reason the transition can be due to Mott instability. TMTTF tetrafluoroborates have the compositions $TMTTF(BF_4)_{0.5}$ (conductor) and $(TMTTF)_x.(BF_4)_y$ ($x/y \cong 1$, dielectric, $\sigma_{300} \cong 2 \times 10^3$ Ω^{-1} m^{-1}).[164]

All the TTF halides contain a more or less large amount of impurities of internal origin due to the disproportionation of the TTF^{+} radical-cation via the mechanism

$$2TTF^{+} \rightleftharpoons TTF^{0} + TTF^{2+} \quad .$$

The random temperature-dependent distribution of impurities stabilises the metallic state[165].

The radical-cation salts of TTT and TST are perhaps of greatest interest at the present time. A whole series of TTT iodides, formed on direct oxidation of TTT with iodine, have been isolated. The iodide (TTT)I is a conductor up to 200 K, while the iodide $(TTT)I_{1.5}$ is a conductor up to 50 K.[166] Studies of the electronic spectra of the crystals and solutions of $(TTT)I_{1.5}$ showed that this salt is the tri-iodide $(TTT)_2^{+}I_3^{-}$,[167] i.e. the degree of oxidation of TTT in this substance is 0.5. The metal–dielectric transition in the salt $(TTT)_2I_3$ has not been observed[168] up to 3.3 K. At 50 K the quantity $\sigma(T)$ passed through a maximum, but the system remained in a conducting state. Subsequently the isolation of the iodide $(TTT)I_{1.6}$ [single crystals, $\sigma_{300} = (7.0–15.0)$ 10^4 Ω^{-1} m^{-1}] was reported[169]. The degree of disorder in this substance is such that the dielectric Peierls transition is suppressed. The situation was clarified after the publication of a study[170] in which it was shown that in reality one should consider the phase $(TTT)I_x$, where x varies from 1.5 to 1.55. With increase of x, the quantity I_{max} diminishes and σ_{max} is greater the smaller the value of T_{max}. At low temperatures there is nevertheless a metal–dielectric transition whose temperature depends significantly on the iodine content. The same workers described a new iodide $(TTT)I_3$ ($\sigma_{300} \cong 50$ Ω^{-1} m^{-1}).

Crystals of the iodide $(TTT)_2I_3$ can be obtained also in the gas phase[171,172], but its structure is not the same as that quoted by Buravov et al.[166] and $T_{max} = 35 \pm 3$ K. Interesting results have been obtained in the calculation of

the Madelung energy of the iodide $(TTT)_2I_3$.[173] Depending on the relative shift of the I_3 ions, this energy has two minima separated by a maximum with $E_a = 4.8 \times 10^{-20}$ J, which gives rise to the possibility of a relative slip of the ions in the $(I_3)_x$ chain with increase of temperature and this leads to structural disorder.

The joint oxidation of TTT with iodine and bromine makes it possible to isolate the mixed salt $(TTT)_2I_xBr_{3-x}$.[174] Qualitatively the $\sigma(T)$ relation is similar to that observed for the pure iodide, but T_{max} is higher, amounting to 150–180 K.

Khidekel' and coworkers[175] obtained TST iodides having the compositions $(TST)I_{0.7-0.8}$, $(TST)I_{1.80-1.85}$, and $(TST)I_{2.2-2.4}$ and an iodide of unknown composition $(TST)I_x$. Khidekel' and Yagubskii and coworkers[176,177] described TST chloride and bromide having the compositions $(TST)_2X$ (X = Cl, Br, or CSN). They are obtained when TST is oxidised by one-electron oxidants (TCNQ, TCNE) in the presence of Cl^-, Br^-, or CSN^- ions. The chloride and bromide are conductors, while the thiocyanate is a semiconductor. Subsequent studies in Shchegolev's laboratory[178,179] on $(TST)_2Cl$ crystals led to the discovery of a phase transition at 25 K of the metal (I)–metal (II) type and of a high-pressure phase at $p > 6 \times 10^8$ Pa, which is also of the metallic type [metal (III), $\rho_{10K} \cong 1.1 \times 10^{-7}$ Ω m]. According to a remark by Shibaeva and Kominskii[133], a common feature of the structures of the complexes (HMTSF)TCNQ and $(TST)_2Cl$ is the interaction between the columns manifested by shortened intermolecular contacts.

The study of the magnetoresistance and the anisotropy of the conductivity of $(TST)_2Cl$ [180] leads to the analogous conclusion, namely that, although, the low-temperature state is strongly anisotropic, its anisotropy is not uniform.

VII. CONDUCTORS BASED ON ORGANOMETALLIC AND COORDINATION COMPOUNDS

Mixed valence platinum complexes have already become traditional objects of study. Apart from the thoroughly investigated platinum cyanide, partly oxidised with chlorine or bromine, highly conducting compounds based on complex oxalates have also been isolated. At the same time conductivity of the metallic type have also been observed, for example, in the compounds $(H_3O)_{1.6}[Pt(C_2O_4)_2]_n.H_2O$ [181] and $K_{1.6}[Pt(C_2O_4)_2].1.2H_2O$; the latter contains, like the complex cyanide $K_{1.75}[Pt(CN)_4].1.5H_2O$ [182,183], a quasi-one-dimensional zig-zag chain of platinum atoms in which there are three crystallographically non-equivalent platinum atoms (Fig. 8). The groups $Pt(C_2O_4)_2$, located at a distance $c/2$, are in the eclipsed configuration and those at a distance $c/4$ are in the staggered configuration. Analogues of the Krogmann salt, namely $(NH_4)_2[Pt(CN)_4]Cl_{0.3}3.2H_2O$ and $(NH_4)_{2.2}.[Pt(CN)_4]Cl_{0.5}.3H_2O$, in which the dielectric Peierls transition occurs at 150 K,[184] and the salt $[C(NH_2)_3]_2[Pt(CN)_4].Br_{0.23}.H_2O$, which exists in the state of a Peierls dielectric even at room temperature[185], have been obtained by exchange reactions. The soliton conduction mechanism is possible for the last salt.

The electrochemical oxidation of the salts $M_2[Pt(CN)_4]$ in the presence of F^- or HF_2^- ions led to the isolation of the following salts from aqueous solutions:

$$K_2[Pt(CN)_4](HF_2)_{0.30} \cdot 3H_2O \quad (I), \quad Rb_2[Pt(CN)_4](HF_2)_{0.40} \quad (II),$$
$$Rb_2[Pt(CN)_4](HF_2)_{0.26} \cdot 1.7H_2O \quad (III), \quad Cs_2[Pt(CN)_4](HF_2)_{0.39} \quad (IV),$$
$$Cs_2[Pt(CN)_4](HF_2)_{0.23} \quad (V), \quad [C(NH_2)_3]_2[Pt(CN)_4](HF_2)_{0.26} \cdot H_2O \quad (VI).$$

The conductivities of salts (II), (IV), and (V), measured on single crystals at room temperature, are respectively 1.6×10^5, 2×10^5, and $(2.5–3.5) \times 10^4$ Ω^{-1} m^{-1}.[186,187] The temperature dependence of the conductivities of certain platinum complexes is illustrated in Fig. 9.

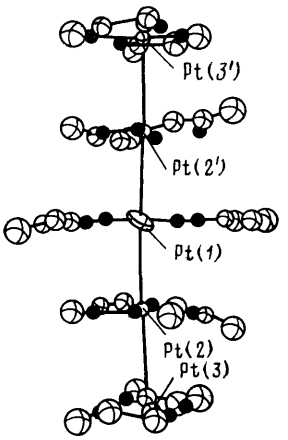


Figure 8. One-dimensional chain of $[Pt(C_2O_4)_2]^{1.6-}$ ions containing three crystallographically non-equivalent Pt atoms[182].

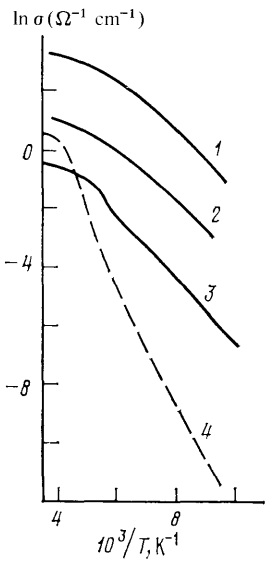


Figure 9. Temperature variation of the electrical conductivity of crystals of complex platinum cyanides: *1*) $K_2[Pt.(CN)_4Cl_{0.3}.3.2H_2O$; *3*) $(NH_4)_2[Pt(CN)_4Cl_{0.3}.3.2H_2O$; *4*) $(NH_4)_{2.2}[Pt(CN)_4]Cl_{0.5}.3H_2O$.[184]

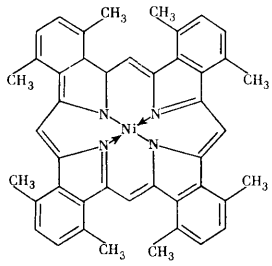
Partially oxidised phthalocyanines and porphyrins form a new class of highly conducting quasi-one-dimensional organic metallic compounds[17,188–191]. Such compounds are obtained, for example, on partial oxidation with iodine of

transition metal (Fe, Co, Ni, Cu, Zn, Pt) complexes of phthalocyanine (Pc):

$$MPc + \frac{x}{2} I_2 \rightleftharpoons (MPc) I_x \quad .$$

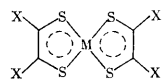
The iodine is present in these compounds mainly in the form of the ion I_3^-; $0.5 \leqslant x \leqslant 3.0$. The conductivity of some of these compounds ($CuPcI_{1.71}$ and $PtPcI_{0.93}$) is comparable to that of the complex $Qn(TCNO)_2$.

The resistance of thin PbPc films decreases with decrease of temperature down to 50 K and remains constant at lower temperatures. Hence the conductivity of porphyrins partly oxidised with iodine increases slightly as the temperature is reduced from 380 to 300 K. After the oxidation of the nickel complex of 1,4,5,8,9,12,13,16-octamethylenetetrabenzoporphyrin, i.e. Ni(OMTBP)



with iodine, the compounds $Ni(OMTBP)(I_3)_y$ with $y = 0.35 \pm 0.03$ and 0.97 ± 0.10 were isolated. The conductivity of the complex with $y = 0.35$ has a maximum at $T \cong 300$ K [$\sigma_{max} = 1.5 \times 10^3\ \Omega^{-1}\ m^{-1}$ (Fig.10)], while for the complex with $y = 0.97$ the maximum is displaced to $T = 340$ K.

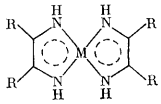
Another interesting class of organometallic compounds forming crystals with a quasi-one-dimensional structure consists of transition metal olefindithiolates with the general formula $M(ODT)_2$ (ODT = olefindithiolate ion having a planar structure with D_{2h} symmetry):



Here M is a transition metal atom and x = alkyl, aryl, CN, CF_3, or H. A characteristic feature of the olefindithiolates is the ease of their one- and two-electron reduction with retention of the planar structure:

$$M(ODT)_2 \overset{+e}{\underset{-e}{\rightleftharpoons}} M(ODT)_2^- \overset{+e}{\underset{-e}{\rightleftharpoons}} M(ODT)_2^{2-} \quad .$$

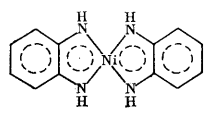
Similar properties are characteristic also of transition metal olefin di-iminates of the same composition:



Five degrees of oxidation are known, for example, for nickel o-phenylene di-iminate:

$$Ni(Pda)^{2+} \overset{+e}{\underset{-e}{\rightleftharpoons}} Ni(Pda)^{+} \overset{+e}{\underset{-e}{\rightleftharpoons}} Ni(Pda) \overset{+e}{\underset{-e}{\rightleftharpoons}} Ni(Pda)^{-} \overset{+e}{\underset{-e}{\rightleftharpoons}} Ni(Pda)^{2-}$$

Ni(Pda) =



All its forms have a planar structure[192].

The use of olefindithiolates and olefin di-iminates for the synthesis of CTC and RIS based on them is doubly interesting, since there is a possibility, in principle, of the formation in such compounds of conducting acceptor or donor columns by the overlap of the d_{z^2} orbitals of the transition metal partly filled as a result of charge transfer. In this sense, they can combine the properties of the mixed valence platinum cyanides (radical-cation salts) and CTC based on TCNQ or TTF.

Some of the complexes of this type which have been isolated do indeed exhibit a high conductivity. For example perylene (PE) forms conducting complexes with nickel, copper, and palladium maleodinitriledithiolates (mnt) having the composition $(Pe)_2^+[M(mnt)_2]^-$ and a thermally activated conducting state [$E_a \cong (1.6\text{–}3.2) \times 10^{-21}$ J].[193] According to Bray and coworkers[194,195], the complex $(TTT)_{1.2}NiS_4C_4H_4$, isolated in the form of black crystals ($\sigma_{298} \cong 3 \times 10^3\ \Omega^{-1}\ m^{-1}$) is a quasi-one-dimensional conductor. Its crystals are formed by one-dimensional TTT chains separated by $[NiS_4C_4H_4]^-$ ions. The degree of filling of the electronic band in this substance is 1/6. The activated nature of the conductivity of the complex ($E_a \cong 1.76 \times 10^{-20}$ J) is due to the presence of the Peierls gap. The electronic and magnetic properties are fully analogous to those of a radical-cation salt.

The complex $(TTF)_2NiS_4C_4H_4$ has been isolated. The complexes of TTF with olefindithiolates have interesting magnetic properties. The magnetic susceptibility of the complexes $TTF[PtS_4C_4(CF_3)_4]$ and $TTF[NiS_4C_4(CF_3)_4]$[196,197] is described by a model consisting of a one-dimensional ferromagnetic with antiferromagnetic interaction between the chains. The peak in the $\chi(T)$ relation at a temperature below 12 K corresponds to the antiferromagnetic ordering. The complex $(TTF)_2[NiS_4C_4H_4]$ is a paramagnetic with single unpaired electrons per molecule.

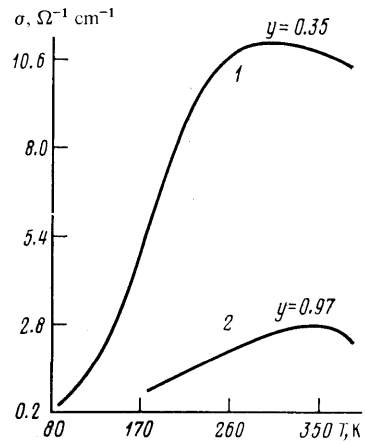
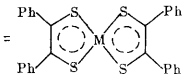


Figure 10. The conductivity of $Ni(OMTBP)(I_3)_y$ crystals: *1*) $y = 0.35$; *2*) $y = 0.97$.[191]

The possibility of the replacement of the central atom in the molecules of olefindithiolates makes it possible to vary their magnetic properties within wide limits. This has been demonstrated in relation to transition metal stilbenedithiolates[198],

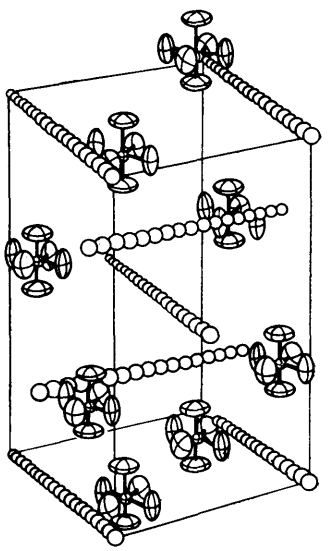
$M(St)_2$ =



M = Fe, Co, Ni .

Nickel stilbenedithiolate is a diamagnetic; the Curie-Weiss law is valid for the susceptibility of $Co(St)_2$ in the range 4–300 K ($\Theta < 1$ K, $\mu_{eff} = 2.06\ \mu_B$), while the susceptibility of the complex $Fe(St)_2$ is described by a model consisting of a one-dimensional Heisenberg antiferromagnetic with a low-temperature increase of $\chi(T)$ due to the finite chain length[198].

The study of the magnetic properties of the complexes $TTF[MS_4C_4(CF_3)_4]$ (M = Cu or Au) led to the discovery of a fundamentally new phenomenon—the spin-Peierls transition[199–201], theoretically predicted by Pytte[202]. The susceptibilities of both complexes have a broad maximum at $T \approx 50$ K; for $T = 12$ K (M = Cu) and 2.1 K (M = Au), the quantity $\chi(T)$ diminishes smoothly. This decrease is described satisfactorily by the theory of the one-dimensional Peierls transition in an antiferromagnetic Peierls chain. At $T < Tp$ new crystalline phases of the complexes contain paired TTF groups with a spin $S = 1/2$.



○ Hg atom ⊕ As atom ⊕ F atom

Figure 11. The crystal structure of $Hg_{2.86}AsF_6$.

Perhaps the most interesting properties among inorganic highly anisotropic compounds are shown by mixed-valence mercury salts[203–210]. In liquid sulphur dioxide direct interaction of mercury with stoichiometric amounts of AsF_5 yields the salts $Hg_3(AsF_6)_2$ and $Hg_4(ASF_6)_2$. The two salts contain linear discrete mercury polycations Hg_3^{2+} and Hg_4^{2+} respectively. The Hg_3^{2+} cation is also present in the salt $Hg_3.(AlCl_4)_2$.[211] Golden crystals with the composition $Hg_{2.85}.AsF_6$ sparingly soluble in SO_2 are formed in the initial stage of the interaction of mercury with AsF_5. The same compound is a product of the disproportionation of the salt $Hg_4(AsF_6)_2$ on slow cooling of its solution in SO_2:

$$5.44Hg_4(AsF_6)_2 \rightarrow 3.44Hg_3(AsF_6)_2 + 4Hg_{2.86}AsF_6 \downarrow .$$

A compound with a similar cation is also obtained on oxidation of mercury with antimony pentafluoride; it has the composition $Hg_{2.91}SbF_6$. The formal degrees of oxidation of mercury in these salts are 0.35 and 0.34 respectively. A characteristic feature of the crystal structures of the two salts is the presence of infinite intersecting linear chains of mercury atoms arranged in two mutually perpendicular directions (Fig. 11). A consequence of this structure is the quasi-one-dimensional behaviour of the salt crystals at the macroscopic level. The bond length in the Hg–Hg chain (2.64×10^{-10} m) is much shorter than in metallic mercury (3.005×10^{-10} m) and is not comparable to the lattice period of the salt. However, the distance between the mercury chains is only 3.085×10^{-10} m, which gives rise to the possibility of an appreciable interaction between the chains.

Thus the systems described possess all conditions for the establishment of the one-dimensional metallic state. The conductivities in the basal planes of the $Hg_{2.86}AsF_6$ and $Hg_{2.91}SbF_6$ crystals σ_{ab} (300 K) are respectively 8.7×10^5 and $\sim 10^5\ \Omega^{-1}\ m^{-1}$. The anisotropy of the conductivity of the $Hg_{2.86}AsF_6$ crystal is $\rho_{ab}/\rho_c \approx 70$ at room temperature. The quantity ρ_{ab} for this salt decreases unusually rapidly on cooling and $\rho_{ab} \approx 10^{-9}\ \Omega$ m already at 4.2 K, which is less than the limit of the measurement. Extrapolution of the $\rho_{ab}(T)$ relation to the absolute zero reveals the absence of a residual resistance. The resistance ρ_c at 4 K decreases abruptly (over a range of 0.2 K) virtually to zero. The disappearance of this transition in magnetic fields directed both parallel to the basal plane and at right angles to it makes it possible to classify it as a superconducting transition. The critical field is minimal if it is directed along the c axis and at $T = 1.4$ K it amounts to 3.8×10^{-2} Wb m^{-2}. In the "normal" state at temperatures less than 30 K and in a field of 10^{-3} Wb m^{-2} the magnetoresistance increases sharply. For $H \neq 0$, a residual resistance appears in the $\rho_{ab}(T)$ relation. The magnetic susceptibility is almost constant in the range 4–300 K; the specific heat C in the range 1.8–5 K is described by the equation $C = \gamma T + \beta T^3$ with an unusually high value of γ.

The study of the elastic and non-elastic reflection of neutrons in the range 10–300 K reveals a phase transition at 120 K corresponding to the ordering of the rigid chains of mercury atoms. At room temperature the salt crystals consist of a network of one-dimensional chains, in the range 300–120 K parallel chains are ordered, and at 120 K order is established between orthogonal systems of chains. At $T < 120$ K the system is three-dimensional.

VIII. CONCLUSION

The study of the quasi-one-dimensional molecular solids examined in this review, which was begun comparatively recently, has developed so effectively that over a short period it has led to the creation of a new scientific field—the chemistry of quasi-one-dimensional metals, including CTC and RIS as well as inorganic, organometallic, and coordination compounds. The number of new objects increases continuously. During the preparation of the manuscript for the press, communications on the synthesis of olefindithiolates with conductivity of their metallic type were published. The conductivity σ_{300} of $Li_{0.75}[Pt(mnt)_2].2H_2O$ crystals is 30–200 Ω^{-1} cm^{-1} and increases slightly up to 250 K.[212] The electrical conductivity of the complex of perylene with

$[Pt(mnt)_2]$, having the composition $(Pe)_2[Pt(mnt)_2]$ increases on cooling, reaching a maximum at 15 K, $\sigma_{300} = 9 \times 10^3\ \Omega^{-1}\,cm^{-1}$,[213] after which it decreases sharply.

The radical-cation salts are being investigated most vigorously at the present time. This was greatly stimulated by the discovery of the superconductivity of the $(TMTSF)_2PF_6$ crystals[214]. As in the series of the isomorphous salts $(TMTTF)_2^+X^-$, where $X^- = BF_4^-$, ClO_4^-, SCN^-, PF_6^-, or Br^- (examined in detail in a review[215]), which undergo the Peierls transition at $T < 100$ K, in the analogous salts $(TMTSF)_2^+X^-$ ($X^- = NO_3^-$, ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, or TaF_6^-) the metal–dielectric transition is observed at lower temperatures ($T < 20$ K) or is not observed at all [for example, for $(TMTSF)_2ClO_4$].[216–222] The metallic phase can be stabilised by the application of an appropriate pressure. In the metal–dielectric transition, there is an unusually marked increase of conductivity—up to $10^5\ \Omega^{-1}\,cm^{-1}$.[222]

Studies of nuclear magnetic resonance and magnetism established that the transition to the dielectric phase in $(TMTSF)_2PF_6$ is associated with spin density waves. Consequently we have here a new example of the spin-Peierls instability. The set of numerous experimental facts—the unusual increase of σ, a very high magneto-resistance, and non-linear voltage—current characteristics—suggest the occurrence of one-dimensional superconductivity fluctuations in the salts $(TMTSF)_2X$ at $T < 40$ K.[221] In the salt $(TMTSF)_2 \cdot PF_6$ the transition to a superconducting state has been observed at pressures $p > 9 \times 10^8$ Pa and $T_c = 0.9$ K.[218] This is a superconductor of the second kind with very low critical magnetic fields $H_{C_1}^{\perp} = 3 \times 10^{-3}$ Wb m^{-2} and $H_{C_2}^{\perp} = 3.3 \times 10^{-2}$ Wb m^{-2}.[216] The transition temperature diminishes fairly rapidly with increasing pressure; thus at $p = 2.4 \times 10^9$ Pa it is $T_c = 0.19$ K.[219] The $T_c(p)$ relation is approximately linear: $\partial T_c/\partial p = -8 \pm 1$ K Pa^{-1}. At $p = 6.5 \times 10^8$ Pa the superconducting and dielectric phases coexist, since the metal–dielectric transition temperature at this pressure is 6 K.[223]

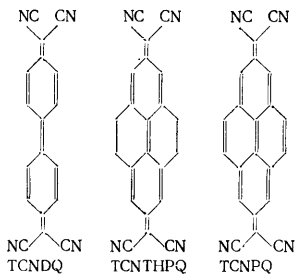
The superconductivity of $(TMTSF)_2AsF_6$ crystals has been observed at $p \geq 1.2 \times 10^9$ Pa and $T_c \leq 1.1$ K.[218] When the pressure is reduced, it is possible to attain $T_c = 1.4$ K at $p = 6.5 \times 10^8$ Pa for the salt $(TMTSF)_2PF_6$ and $p = 10^9$ Pa for the salt $(TMTSF)_2AsF_6$.

The superconductivity of $(TMTSF)_2ClO_4$ ($p = 3 \times 10^8$ Pa), $(TMTSF)_2SbF_6$ ($p = 10^9$ Pa), and $(TMTSF)_2TaF_6$ ($p = 1.1 \times 10^9$ Pa) crystals has been observed[222]. At $p = 10^5$ Pa the superconducting transition in $(TMTSF)_2ClO_4$ is observed at 1.3 K.

Even on the basis of aromatic hydrocarbons, highly conducting radical-cation salts have been obtained and isolated. They have the composition $(Arene)_2^+X^-$, where $X^- = PF_6^-$, AsF_6^-, SbF_6^-, BF_4^-, or ClO_4^- and Arene = naphthalene, fluoranthene, pyrene, perylene, and triphenylene[224]. The salt $(naphthalene)_2^+(PF_6^-)$ exhibits the highest conductivity ($\sigma_{293} = 0.12\ \Omega^{-1}\,cm^{-1}$). Typical conductivities of other salts are in the range 10^{-2}–$10^{-3}\ \Omega^{-1}\,cm^{-1}$.

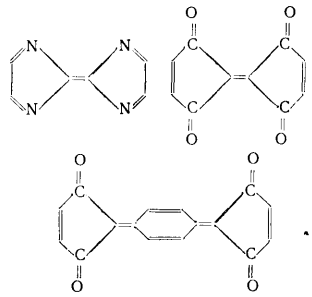
Highly conducting salts of a new donor—tetratellurotetracene (TTeT),—having the composition $(TTeT)_2X$ (X = Cl or Br), were isolated recently[225]. The conductivity σ_{293} of the pelleted specimens is 1–2 $\Omega^{-1}\,cm^{-1}$. The authors were unable to isolate single crystals suitable for the measurement of the electrical conductivity and it is therefore not clear whether the electrophysical properties change significantly following the replacement of sulphur or selenium ions by tellurium.

Publications on the synthesis of new acceptors—tetracyanodiphenoquinodimethane (TCNDQ), tetracyanotetrahydropyrenoquinodimethane (TCNTHPQ), and tetracyanopyrenoquinodimethane (TCNPQ) —have appeared recently[226,227].

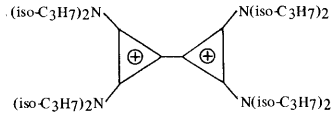


These acceptors form dianions and radical-anions and are apparently stronger acceptors than TCNQ as far as one can judge from their electrochemical potentials. They form CTC with TTF in the form of fine black crystals. However, in our view, acceptors of this kind can hardly be used for the synthesis of compounds with interesting electrophysical properties. It is difficult to select for TCNTHPQ and TCNPQ a donor close to them in linear dimensions, which is one of the conditions for the preparation of CTC of the non-interleaved type[228]. Low solubility is also an obstacle to the preparation of single crystals. Furthermore, in connection with the discovery of the superconductivity of radical-ion salts, the problem of the synthesis of organic superconductors with the highest possible T_c has now become urgent. Apart from the requirements formulated by Krivoshei[228], the components of the CTC or the RIS must satisfy yet another significant condition in order to achieve this[229]: they must exhibit a high polarisability for small linear dimensions.

The synthesis of the acceptors illustrated below is of interest in this sense:



The ways of synthesising such acceptors are being sought nowadays by the authors of the review. The study[230] in which the salt $\{[(iso\text{-}Pr)_2N]_4TF\}^{2+}(ClO_4^-)_2$ (TF = triafulvalene)



was isolated merits attention. The salts of TF and of its substituted derivatives can be used to prepare CTC by exchange reactions (with partial reduction) for the synthesis of RIS.

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