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Spectral studies of new organic conductors based on TTF derivatives with polymeric isocyanuric acid anions

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Spectral investigations of new organic conductors (BEDO-TTF)$_2$($C_3H_2N_3O_3$) and (DB-TTF) ($C_3H_2N_3O_3$) were performed. Optical absorption spectra in the range of 400–40 000 cm^{-1} of the powdered salts dispersed in KBr pellets were recorded and analysed. The spectra of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) are characteristic of organic metals and show small anisotropy, which is typical of quasi-two-dimensional materials. On the other hand, the spectra of (DB-TTF)($C_3H_2N_3O_3$) are typical of semiconducting materials. The (BEDO -TTF)$_2$($C_3H_2N_3O_3$) salt undergoes a phase transition at about 120 K. The polarized reflectance spectra of single crystals of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) were recorded in the range of 600–7000 cm^{-1}, down to 4 K. The frequency dependences of reflectivity were fitted with a Drude model and the transport parameters were evaluated and investigated vs. temperature. An assignment of some vibrational bands in the IR spectra was proposed.

Key words: *BEDO-TTF salt; DB-TTF salt; TTF derivatives; organic conductors; IR spectroscopy; transport properties*

1. Introduction

Most of the research concerning organic conductors has been focused on the synthesis and studies of cation radical salts based mainly on the bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF or ET) molecule and its numerous structural modifications. For our spectral investigations we chose new salts formed by bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) and dibenzotetrathiafulvalene (DB-TTF) donors, with a monosubstituted anion of isocyanuric acid $(C_3H_2N_3O_3)^-$ (Scheme 1).

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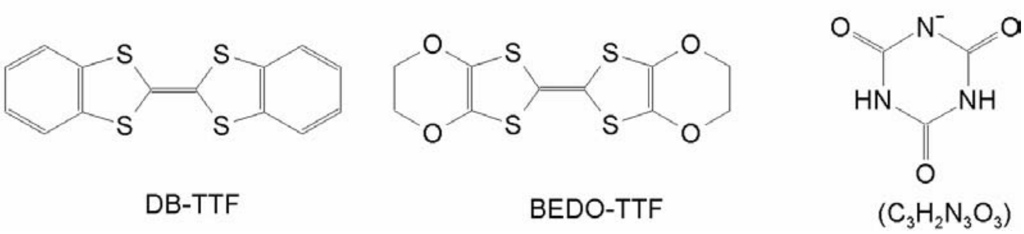

Scheme 1. The DB-TTF molecule, BEDO-TTF molecule and $(C_3H_2N_3O_3)^-$ isocyanuric acid anion

BEDO-TTF and DB-TTF are modifications of the BEDT-TTF molecule; the difference between these molecules lies in their outer rings. The BEDO-TTF molecule, with four sulphur atoms in the outer rings substituted by oxygen atoms, is a well-known donor molecule that has been successfully used for the synthesis of many ion-radical salts exhibiting metallic conductivity and superconductivity [1–4]. The DB-TTF molecule is less commonly used; instead of two outer rings with ethylenedithio fragments, it contains two outer benzene rings. The carbon atoms in the benzene rings are smaller than sulphur (in BEDT-TTF) or oxygen atoms (in BEDO-TTF), which strongly influences physical properties of DB-TTF salt compared to the salts of BEDT-TTF and BEDO -TTF.

Similar to (BEDT-TTF)$_2$($C_3H_2N_3O_3$) [5], the crystal structure of (BEDO-TTF)$_2$-($C_3H_2N_3O_3$) has a layered arrangement; the BEDO-TTF layers alternate with $(C_3H_2N_3O_3)^-$ anions. In DB-TTF salt, one can observe one-dimensional stacks. As in (BEDT-TTF)$_2$($C_3H_2N_3O_3$) [5], the anions in (BEDO-TTF)$_2$($C_3H_2N_3O_3$) and (DB-TTF)($C_3H_2N_3O_3$) are also linked by hydrogen bonds in one-dimensional polymer chains, which do not interact with each other. (BEDO-TTF)$_2$($C_3H_2N_3O_3$) is a 2D metal-like conductor down to 120 K (σ_{RT} =3.34 S/cm); at this temperature the salt undergoes a phase transition. (DB-TTF)($C_3H_2N_3O_3$) salt, on the other hand, exhibits semiconducting properties with a room temperature conductivity of $\sigma_{RT} = 10^{-1}$ S/cm [5].

In this communication, we report the first spectral studies of (BEDO -TTF)$_2$($C_3H_2N_3O_3$) and (DB-TTF)($C_3H_2N_3O_3$) salt. The aim of these investigations is to obtain information on the physical properties of these salts over broad spectral and temperature ranges.

2. Experimental

Crystal preparation by electrocrystallization has been described elsewhere [5]. The typical dimensions of the single crystals selected for spectral investigations were about $0.02 \times 0.5 \times 1.0$ mm^3 for BEDO-TTF salt and $0.02 \times 0.1 \times 2.0$ mm^3 for DB-TTF salt. Samples of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) crystallize in the form of elongated plates with flat and reflecting faces, whereas (DB-TTF)($C_3H_2N_3O_3$) crystallizes in the form of needles. The DC conductivity of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) was measured by a standard DC four-probe technique down to the helium temperature.

The near normal polarized reflectance spectra of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) salt for frequencies in the range of 600–7000 cm^{-1} were investigated as a function of temperature (4–300 K). The spectra were recorded from the best-developed crystal face, parallel to the conducting layers, using a FT-IR Perkin Elmer 1725X spectrometer equipped with a suitable IR microscope and cryostat. The spectra were measured for two mutually perpendicular polarizations of the incident IR beam, corresponding to the maximum ($E_{\max}$) and minimum ($E_{\min}$) of the reflected energy. For low-temperature measurements, the samples were mounted in an Oxford Instruments helium cryostat, connected to a temperature controller. The plasma-edge-like dispersion in the reflectance spectra was fitted with a Drude dielectric function. Temperature dependences of optical transport parameters (plasma frequency – ω_p, relaxation rate – Γ, and all higher frequency contributions to the dielectric function – ε_∞) were investigated. Additionally, we studied the absorption spectra of powdered samples of both BEDO-TTF and DB-TTF salts dispersed in KBr pellets in the frequency range of 400–40 000 cm^{-1}, at room temperature. These investigations were performed with two spectrometers: a Bruker Equinox 55 and a UV/Vis/NIR Perkin Elmer Lambda 19.

3. Results and discussion

3.1. Electronic structure

The electronic and vibrational absorption spectra of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) and (DB-TTF)($C_3H_2N_3O_3$) salts are shown in Fig. 1.

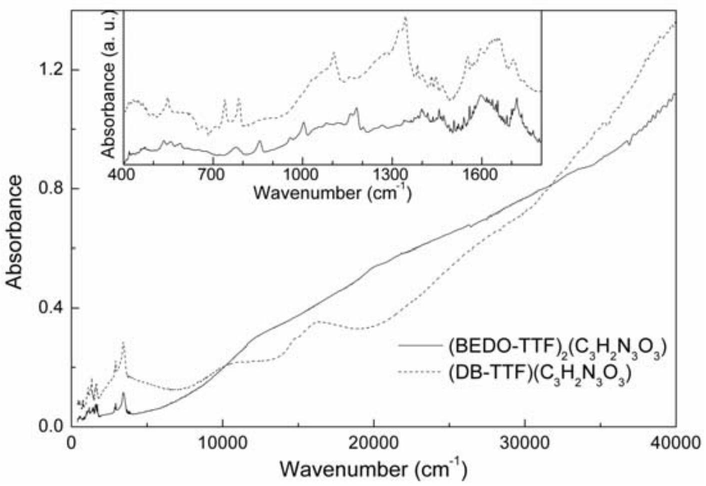

Fig. 1. Electronic absorption spectra of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) and (DB-TTF)($C_3H_2N_3O_3$) powders dispersed in KBr pellets (weight concentration 1:2000). The inset shows the vibrational part of the absorption spectrum

The spectrum of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) consists of intermolecular charge transfer bands at about 3000 cm^{-1} and 12 200 cm^{-1}, and a band related to intramolecular excitations at about 20 000 cm^{-1}. The band at 3000 cm^{-1} corresponds to the charge transfer process BEDO-TTF^0 + BEDO-TTF$^+$ → BEDO-TTF$^+$ + BEDO-TTF^0 [6]; its position depends on the hopping integrals and the Coulomb repulsion energy between two electrons on adjacent molecules. The band at 12 200 cm^{-1} is attributed to the charge transfer process BEDO-TTF$^+$ + BEDO-TTF$^+$ → BEDO-TTF^{2+} + BEDO-TTF^0 [7]. The position of this band can be described approximately by the value of the effective Coulomb interaction, which is given by $U = U_0 - V_1$, where U_0 is the intramolecular Coulomb repulsion energy between two electrons on the same site. The most important difference between the electronic spectra of BEDT-TTF and BEDO-TTF reveals itself in the position of the mentioned intermolecular band at about 12 000 cm^{-1}; it is observed in BEDT-TTF salt at a lower frequency, namely around 10 000 cm^{-1}. It results from calculations of valence force constants that the rigidity of the outer rings of BEDO-TTF is larger than that of BEDT-TTF [8]. This can lead to a less effective screening of Coulomb interactions and an increase in both U_0 and the frequency of this charge transfer band. The spectrum of (DB-TTF)($C_3H_2N_3O_3$) consists of bands at about 3400 cm^{-1}, 11 000 cm^{-1}, 16 500 cm^{-1}, and 28 000 cm^{-1}. By analogy to BEDT-TTF compounds (see e.g. [7]), we relate the first two bands to intersite charge transfer excitations, whereas the bands at 16 500 cm^{-1} and 28 000 cm^{-1} to the intramolecular excitation of the DB-TTF molecule.

The reflectance spectra of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) salt at 300 K and 40 K, for two perpendicular polarizations, are displayed in Figs. 2 and 3.

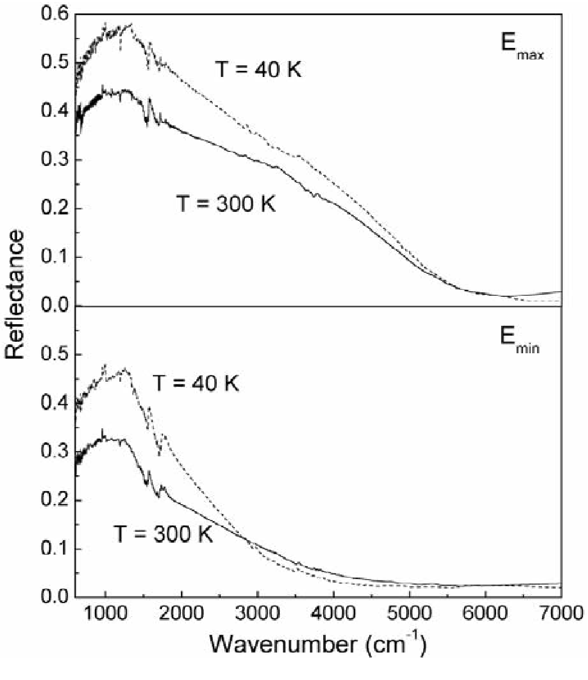

Fig. 2. Polarized reflectance spectra of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) single crystals at 300 K and 40 K for two perpendicular polarizations, E_{max} (upper panel) and E_{min} (lower panel)

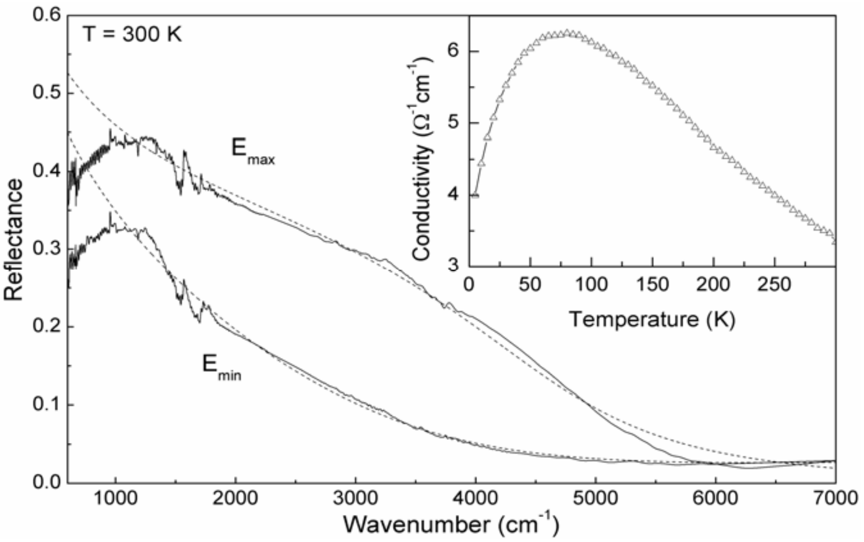

Fig. 3. Polarized reflectance spectra of (BEDO-TTF)$_2$(C$_3$H$_2$N$_3$O$_3$) single crystals at room temperature for two perpendicular polarizations, $E_{\max}$ and $E_{\min}$, of the IR beam (dotted lines represent the Drude fits). The inset shows the temperature dependence of electrical conductivity for (BEDO-TTF)$_2$(C$_3$H$_2$N$_3$O$_3$)

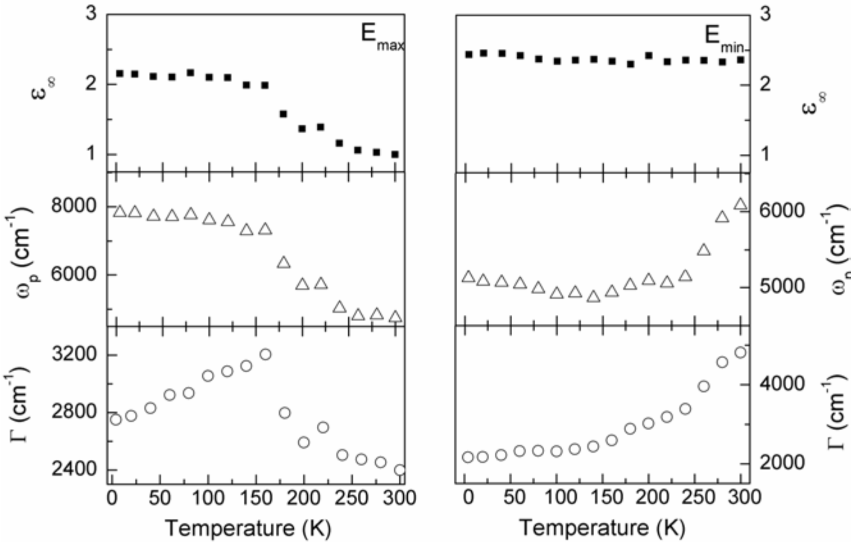

Fig. 4. Temperature dependences of the Drude parameters, extracted from fitting the reflectance data of (BEDO-TTF)$_2$(C$_3$H$_2$N$_3$O$_3$) crystals for two perpendicular polarizations, $E_{\max}$ and $E_{\min}$, of the IR beam; ω_p is the plasma frequency, ε_∞ represents all higher frequency contributions to the dielectric function, and Γ is the damping constant, which is related to the relaxation time of carriers τ ($\Gamma = 1/c\tau$, c is the speed of light)

The electronic dispersion observed below about 6000 cm^{-1} is characteristic of compounds showing metallic properties; it is in agreement with electrical conductivity measurements (see the inset in Fig. 3). The observed plasma-like dispersion authorized us to use the Drude model for calculating the plasma frequency ω_p and relaxation rate Γ. Least squares fits to the experimental reflectance in the range of 2000–7000 cm^{-1} (not taking into account the region of vibrational bands, which could perturb the fit parameters) were made for reflectance calculated from the Drude dielectric function $\varepsilon(\omega) = \varepsilon_\infty - \omega_p^2 / \omega(\omega + i\Gamma)$. The results of the fitting procedure at room temperature, for the two perpendicular polarizations of the IR beam $E_{\max}$ and $E_{\min}$, are shown in Fig. 3. The temperature dependences of the transport parameters, determined by the Drude analysis, are presented in Fig. 4.

The phase transition in (BEDO-TTF)$_2$(C$_3$H$_2$N$_3$O$_3$) considerably influences the band structure parameters. When decreasing the temperature down to about 140 K, the relaxation rate Γ and plasma frequency ω_p grow for a polarization of $E_{\max}$ and decrease for a polarization of $E_{\min}$. Below 140 K, the plasma frequency ω_p slightly grows with decreasing temperature, whereas the relaxation rate Γ decreases. Such a behaviour of the transport parameters can be related to an increase in transfer integrals, in turn resulting from a reduction of the unit cell volume at lower temperatures. It should be emphasized that the phase transition in (BEDO-TTF)$_2$(C$_3$H$_2$N$_3$O$_3$) is smeared over a broad temperature range in electrical conductivity measurements, and is observed at temperatures lower than the phase transition temperature determined from spectroscopic data. The modification of the transport parameters in this salt can be explained by a redistribution of charge density, and by an increase of the fraction of localized charges due to a decrease in the interactions between the BEDO-TTF molecules of neighbouring stacks.

3.2. Vibrational structure

Compared to the vibrations of the BEDT-TTF molecule [9], a normal coordinate analysis of BEDO-TTF [8] shows that the substitution of sulphur by oxygen in the outer rings leads to a markedly different charge distribution. The charge densities on the central C$_2$S$_4$ fragments of both molecules are practically the same but important differences are observed in the outer rings; the strongly electro-negative oxygen almost completely gathers the electron density of the carbon atoms. Many bands, especially those related to C-O-C fragments, therefore appear at shifted frequencies. The presence of the oxygen atoms also leads to a sharp increase in electron-molecular vibration (EMV) coupling for totally symmetric A_g modes related to the outer rings [8].

The infrared spectrum is useful for evaluating the ionicity of the ground state of CT complexes, and the degree of CT from donor to acceptor molecules. It can be estimated by utilizing specific vibrational frequencies which are sensitive to the ionicity of the molecule [10]. Moldenhauer et al. [11] have reported that the four absorption bands of BEDO-TTF^0 (864, 963, 1011, and 1082 cm^{-1}) display distinct ionisation frequency shifts on CT complex formation. According to the normal coordinate analysis of the neutral BEDO-TTF molecule, the above four bands involve vibrations of C-O bonds [8]. In this work concerning (BEDO-TTF)$_2$($C_3H_2N_3O_3$) single crystals, the appropriate bands are observed at 856, 956, 1000, and 1078 cm^{-1}. Taking into account this result [11], we estimate that the average charge per donor molecule in the salt is +0.5e.

The most characteristic feature of the IR spectra of BEDO-TTF salt is the large red shift of the ring C=C stretching band upon oxidation which appears between 1646 cm^{-1} (neutral BEDO-TTF) and 1456 cm^{-1} (BEDO-TTF^{2+}). These peaks may be assigned to BEDO-TTF in a partly oxidized state, especially the peak appearing at 1527 cm^{-1} (Fig. 1) was assigned to the C=C stretching in BEDO-TTF^{+} [12]. The IR spectra of (BEDO-TTF)$_2$($C_3H_2N_3O_3$) salt are much richer than those of BEDO-TTF; Shinohara et al. [6] have observed a similar effect. Different absorption wavenumbers from that of BEDO-TTF also imply that new electronic states appear, different from those of neutral BEDO-TTF.

4. Conclusions

In this paper, the spectra of two new salts, namely (BEDO-TTF)$_2$($C_3H_2N_3O_3$) and (DB-TTF)($C_3H_2N_3O_3$), were presented and preliminarily discussed for the first time. An analysis of the spectra allowed us to obtain information about their electronic and vibrational properties. The spectral data confirm the presence of a phase transition in (BEDO-TTF)$_2$($C_3H_2N_3O_3$) at about 120 K. Subsequent investigations of the salts will be published soon.

Acknowledgements

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