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FT-IR INVESTIGATIONS OF BEDO-TTF AND RADICAL SALTS OF BEDO-TTF

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Abstract

We investigated powder absorption spectra of the donor BEDO-TTF and some radical salts of BEDO-TTF, which are metals even at low temperatures. After an assignment of the bands in the neutral donor we found in the radical salts different vibrational frequencies of bands correlated with C–O vibrations. These frequencies are directly related to the average charge on the donor molecule. Additionally frequencies of CH_2-stretching vibrations exhibit differences, which can be ascribed to a varying strength of donor-anion interaction depending on the respective anion.

Introduction

The successful history of radical cation salts of the organic donor BEDT-TTF (bis(ethylenedithiolo)tetrathiafulvalene) concerning metallic conductivity and superconductivity with T_c up to 12.5 K [1] has always produced attempts towards modifying this donor. One modification consists in the substitution of the outer sulfur atoms through oxygen, yielding BEDO-TTF (bis(ethylendioxy)tetrathiafulvalen) (Fig. 1), which was synthesized for the first time by Suzuki et al. [2]. The aim in this substitution was twofold [3] : Firstly BEDO-TTF as a constituent in a radical cation salt now contains lighter atoms than BEDT-TTF, therefore raising T_c according to BCS-theory, and secondly a smaller conduction bandwidth was

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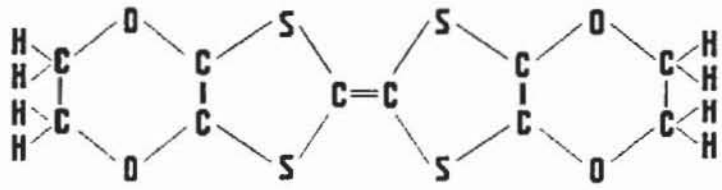
expected, which should increase the density of states near the Fermi level. In the meantime a lot of radical cation salts have been synthesized, two of them exhibiting ambient-pressure superconductivity – $(BEDO\text{-}TTF)_3Cu_2(NCS)_3$ [4] with $T_c = 1.06$ K and $(BEDO\text{-}TTF)_2\ ReO_4{\cdot}H_2O$ [5] with an onset of superconductivity at 2.5 K.

Fig. 1.
The BEDO-TTF molecule



The aim of the spectroscopic work on the neutral donor BEDO-TTF and a few radical cation salts of it was an assignment of the fundamental vibrations of BEDO-TTF according to the assignment of BEDT-TTF (recently a normal coordinate analysis has been carried out by Pokhodnia et al. [6]), an investigation of the dependence of vibrational frequencies on the average charge per donor molecule and of the behaviour of the CH_2-stretching frequencies in different salts.

Experimental

The donor BEDO-TTF was synthesized as described by Suzuki et al. [2], the crystals of the radical cation salts investigated in this work have been prepared electrochemically using the crown ether route [7]. For infrared absorption measurements, 0.8 mg of crystals were ground with 200 mg KBr in an agate mortar and afterwards pressed to pellets with a pressure of $9\,t/cm^2$.

The spectra were taken on a commercial Fourier transform spectrometer (BOMEM DA 3.02) with a fast InSb detector in the range of 5000 – 1800 cm^{-1} and a MCT detector between 1800 cm^{-1} and 450 cm^{-1} – the applied resolution was 0.5 cm^{-1}. In order to obtain a good signal-to-noise ratio, 2000 interferograms were coadded for each spectrum.

Results

A. The molecular vibrations of the donor BEDO-TTF.

The vibrational bands of BEDO-TTF in the range between 450 cm^{-1} and 1750 cm^{-1} are shown in Fig. 2, the insert displays the CH_2-stretching vibrations around 3000 cm^{-1}.

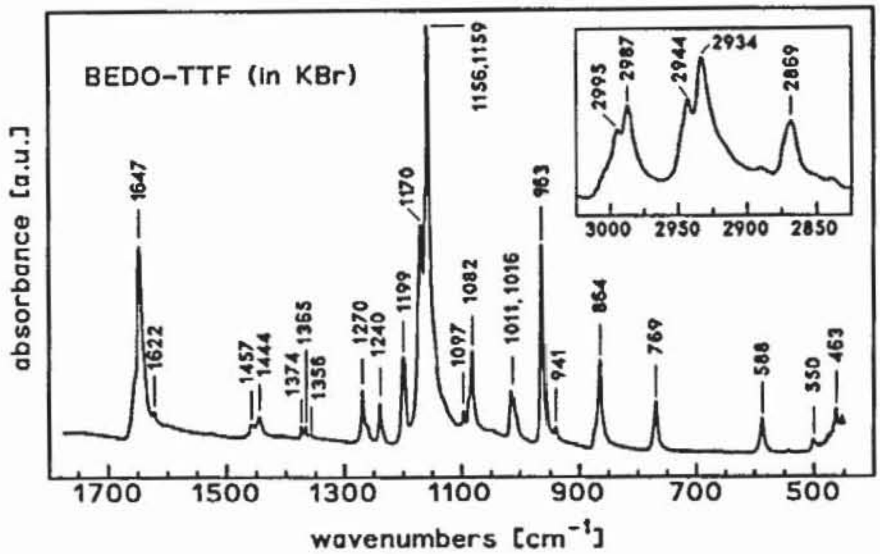


Fig. 2. Vibrational spectrum of BEDO-TTF in KBr

Comparing with the vibrations of BEDT-TTF [8], the normal coordinate analysis in [6] shows that the substitution of sulfur by oxygen in the outer rings leads to a strongly different distribution of the charge on the molecule as in the latter. Therefore many bands are expected to appear with different frequencies, especially when the C–O–C-groups are involved in the respective fundamental vibration. Apart from these vibrations we observe mainly two remarkable facts: First of all the CH_2-groups are only slightly affected by this redistribution with respect to BEDT-TTF – the frequency shift of their stretching vibration (i.e. vibrations with no other bonds involved) is less than 1%. On the other hand, there is a strong change in the vibrations of the C=C-bonds in the center and in the rings – whereas the symmetric stretching of the central C=C-bond (Raman active) is only sligthly shifted upwards by ≈ 2%, the shift of the in-phase as well as of the anti-phase stretching of the ring C=C amounts ≈ 150 cm^{-1} or nearly 10 %.

This fact should strongly affect the frequencies of the appearing vibronic band in the radical salts of BEDO-TTF, which in the observed frequency range are caused by the latter mentioned in-phase vibration inducing a coupling of the radical electrons to this vibration.

B. The molecular vibrations of radical cation salts $(BEDO\text{-}TTF)_mX_n$

Aside from the above mentioned salts with superconducting phase transitions $(BEDO\text{-}TTF)_3Cu_2(NCS)_3$ and $(BEDO\text{-}TTF)_2ReO_4{\cdot}H_2O$ we investigated as well $(BEDO\text{-}TTF)_{2.4}I_3$ [3] and a BEDO-TTF chloride phase, which both exhibit metallic behaviour. The exact composition of the investigated BEDO-TTF chloride phase is not known because of the poor crystal quality. This phase is designated as "$(BEDO\text{-}TTF)_2Cl$" in Figs. 3 and 4 because of the IR data dicussed below.

The absorption spectra of different radical salt of BEDO-TTF between 1800 and 600 cm^{-1} are shown in Fig. 3. The overall structure is the same for all spectra (except for the presence of a band at 910 cm^{-1} in the ReO_4-salt, which is due to a vibration of the anion) – the prominent features are the broad bands around 1600 cm^{-1}, and a few remarkably strong bands between 1200 and 800 cm^{-1}. According to the normal coordinate analysis for the neutral BEDO-TTF [6], most of the latter are due to vibrations including C–O bonds. The assignments presented there as well give an explanation for the origin of the broad bands mentioned before: They have to be taken as vibronic bands due to EMV coupling, as this was already discussed [9] for BEDT-TTF salts.

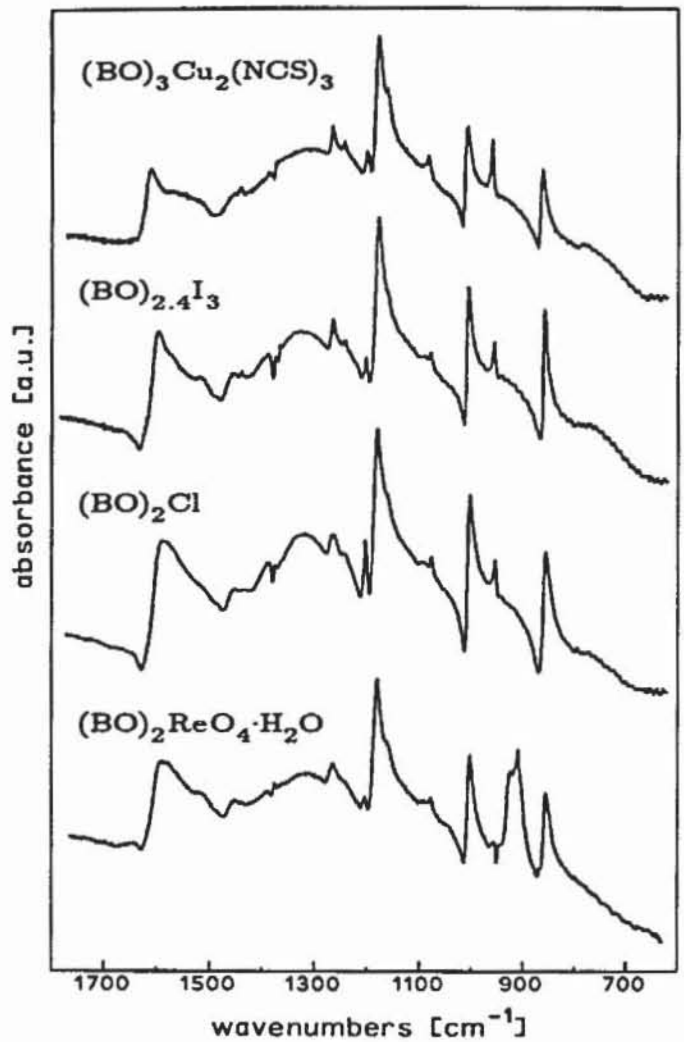
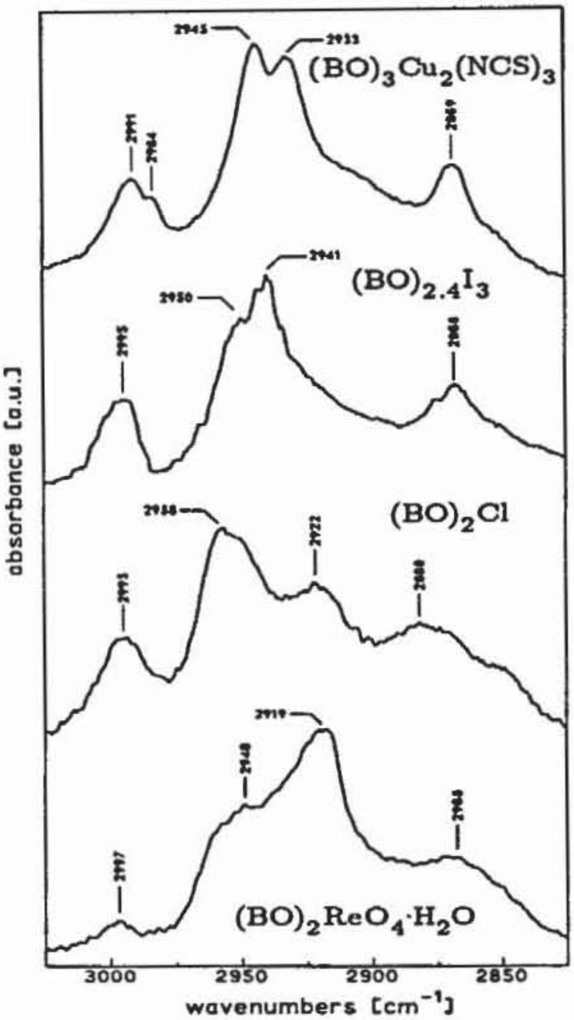


Fig. 3. IR absorption spectra of radical cation salts of BEDO-TTF (abbreviated as BO)

A closer examination of the frequencies of all these mentioned bands is given in the subsequent discussion.

C. CH_2-stretching vibrations

Concerning the above mentioned different average charge on the donor molecules, ranging from +0.33 to +0.5 in the different investigated salts, it could be shown [10] in radical salts of BEDT-TTF, that the frequencies of the CH_2-stretching vibrations are nearly unaffected by the respective charge per donor molecule. A comparison with those of BEDO-TTF shows, that a substitution in the outer rings as in the present case causes a shift to higher frequencies of nearly 1%, but the behaviour after ionization is exspected to be the same as in BEDT-TTF. The shifts observed in these radical salts are rather due to the donor-acceptor interactions, which are mediated by the terminal ethylene groups, as long as the anions are lying in sheets separating the donor stacks.



In turning our attention to the CH_2-stretching vibrations in radical salts of BEDO-TTF, which are shown in Fig. 4 (a baseline correction has been applied), we first of all should compare the observed bands with those found in neutral BEDO-TTF. In (BEDO-TTF)$_3$ $Cu_2(NCS)_3$ the observed differences are very small, increasing on going from the iodine salt to the 2:1 salts. Refering to the situation found in BEDT-TTF it is worth noting, that in neutral BEDO-TTF the interaction between the molecules is determined by short C–H···O contacts [11] and it is reported – at least for (BEDO-TTF)$_3$$Cu_2(NCS)_3$ [4] and the iodine salt [3], that these contacts are dominating the packing motifs even of the radical salts.

Fig. 4. CH_2-stretching bands of BEDO-TTF (abbreviated as BO) radical salts

D. Conclusions

The CH_2-stretching vibrations therefore indicate an increasing interaction on going from an anion with weaker or more diluted electronegative constituents like $Cu_2(NCS)_3^-$ to anions with a higher electron affinity like Cl^- and ReO_4^-. But a stronger interaction of CH_2-groups with electronegative anions like the latter means presence of an at least weak hydrogen bonding, which should decrease the frequency of CH_2-stretching vibrations. Concerning the most intensive bands we observe both a shift to higher frequencies as well as to lower. Therefore we propose, that the strong donor-donor interaction via C–H···O contacts (as known from neutral BEDO-TTF) is a strong competitor for donor-anion contacts as long as the electronegativity of the anions is small. This might be as well the reason for the fact that in the iodide-salt and (BEDO-TTF)$_3$$Cu_2(NCS)_3$ an incommensurable sublattice and a commensurable superlattice respectively is found.

On the other hand, donor-donor interactions are surely influenced by the average charge on the donor. Significant dependencies of vibrational frequencies of several fundamental modes are given in Fig. 5 – it should be noted, that all these modes involve vibrations of C–O bonds. From the decrease in frequencies it is

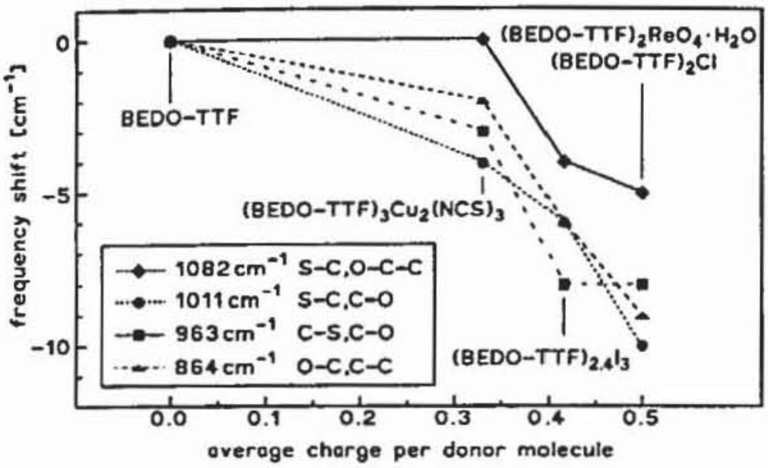


Fig. 5.

Dependence of frequency shifts of several vibrational modes (with respect to BEDO-TTF) on the average charge per donor molecule. The applied resolution was $0.5\,cm^{-1}$.

clear, that the transferred charge mainly stems from the π-electron framework contributed by oxygen atoms. The fact that the observed shifts of $(BEDO\text{-}TTF)_2$ $ReO_4{\cdot}H_2O$ and of the investiged BEDO-TTF chloride salt are identical supports the assumption of an identical stoichiometry for the chloride phase.

Additionally some information about the donor-donor interaction can be extracted from the positions of the vibronic band, which range from $1610\,cm^{-1}$ to $1585\,cm^{-1}$. But for a reliable interpretation the Raman spectra of the radical salts in question are necessary, which are not available yet.

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