Electrical and Spectral Properties of Organic Salts Formed from BEDT-TTF and Magnetic Anions

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Summary: Spectral and electrical investigations of the semiconducting (BEDT-TTF)$_2$W$_6$O$_{19}$ and the metal-like (BEDT-TTF)$_6$(Mo$_8$O$_{26}$)(DMF)$_3$ salts were performed. The vibrational and electronic spectra of the crystalline samples were analysed and assignment of the vibrational features was proposed. The temperature evolution of the vibrational spectra of the (BEDT-TTF)$_2$W$_6$O$_{19}$ salt was discussed.

Keywords: BEDT-TTF salts; charge transfer; infrared spectroscopy; polyoxometalate anions; UV-vis spectroscopy

Introduction

Recently, much attention was devoted to exploration of the novel lattice architectures and physical properties resulting from the association of organic cation radicals, such as BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) with bulky anions (e.g. polyoxometallates[1]). One of the reasons for the interest in polyoxometalate-based materials, containing both localized and delocalized electrons is the possibility of formation of compounds where the coexistence of co-operative magnetic and electric properties such as ferromagnetism and superconductivity can be observed.[2] Moreover, Coulomb interactions between organic (cations) and inorganic (anions) subsystems may also induce a partial charge transfer (CT) which can lead to an increasing electrical conductivity through the anionic system.

These hybrid materials are usually built of alternating organic and inorganic layers. The organic layers are created by peculiar arrangement of BEDT-TTF species with short intermolecular contacts. The inorganic ones are formed from polyoxometalate anions and solvent molecules (if they occur). The polyoxometallate structures are made by the association of MO_6 octahedra (where M is Mo, W, Nb).[3-9] Both organic and inorganic

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building blocks show a structural disorder which is so important for the electron distribution in these blocks.

A detailed spectral investigation of a crystal belonging to this type of compounds, (BEDT-TTF)$_2$Mo$_6$O$_{19}$, has been recently published by Visentini et al.[9] In this salt, the fully oxidised organic species (BEDT-TTF$^+$) overlap in an eclipsed geometry and form quasi-isolated dimers.[4] According to our studies, the crystals show semiconducting properties similar to those of (TTF)$_2$Mo$_6$O$_{19}$.[6]

The crystal structure of the (BEDT-TTF)$_2$W$_6$O$_{19}$ salt, which is isostructural with (BEDT-TTF)$_2$Mo$_6$O$_{19}$, was described by Triki et al.[5] The inorganic layers of the salt are formed by $(W_6O_{19})^{2-}$ polyanions, which are members of a group of discrete isopolymetallates having a Lindquist-type structure.[10] The orthogonalized dimers of (BEDT-TTF)$^+$ cations form the organic layers. The electrical conductivity investigations performed by Kravchenko et al.[11] showed that (BEDT-TTF)$_2$W$_6$O$_{19}$ is a narrow-gap semiconductor (E_a = 0.17 eV). Its conductivity (measured in pellet, at room temperature) is between 0.07 and 0.12 S·cm^{-1}. The preliminary IR spectra of the salt have been also presented.[11]

The electrochemical preparation and characterisation of the (BEDT-TTF)$_6$(Mo$_8$O$_{26}$)(DMF)$_3$ salt have been recently reported by us.[12] Inorganic layers of this salt are formed from $(Mo_8O_{26})^{4-}$ anions and dimethylformamide (DMF) molecules. Organic layers are built from planar and non-planar BEDT-TTF units, which are organised in two types of step-chains. The d.c. electrical conductivity of the crystalline sample of (BEDT-TTF)$_6$ (Mo$_8$O$_{26}$)(DMF)$_3$ is about 3 S·cm^{-1} at room temperature, increasing gradually down to 60 K, where it amounts to a value of about 12 S·cm^{-1}. Below this temperature, the conductivity decreases rapidly reaching at 4 K the value five orders lower than at about 300 K.[12] The low-temperature range can be described by a hopping model but the conductivity at $T > 60$ K reveals a metal-like character. IR and Raman spectra of (BEDT-TTF)$_6$(Mo$_8$O$_{26}$)(DMF)$_3$ single crystals were also analysed.[12]

This work reports mainly the extended IR spectral investigations of the semiconducting (BEDT-TTF)$_2$W$_6$O$_{19}$ salt. Its properties are discussed and compared with the data for the hybrid semiconducting (BEDT-TTF)$_2$Mo$_6$O$_{19}$[9] and metal-like (BEDT-TTF)$_6$(Mo$_8$O$_{26}$)(DMF)$_3$[12] salts recently published.

Experimental

Black crystals of (BEDT-TTF)$_2$W$_6$O$_{19}$ salt with submillimetre dimensions were obtained on a smooth platinum wire electrode by anodic oxidation of solution of organic donor BEDT-TTF in the presence of a background salt. More details of preparation of the salt were given by

Kravchenko et al.[11] The procedure of preparation of $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ from DMF solution by anodic oxidation under galvanostatic conditions was described elsewhere.[12]

For d.c. electrical conductivity measurements, bar-shaped crystals of both $(BEDT\text{-}TTF)_2W_6O_{19}$ and $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ salts were selected. The conductivity was measured along the long axis of the crystals, using a standard four-probe technique.[12]

Absorption spectra of $(BEDT\text{-}TTF)_2W_6O_{19}$ and $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ in KBr pellets were recorded in the range 400 - 45000 cm^{-1} with a Perkin Elmer UV-VIS-NIR Lambda 19 and FT IR Perkin Elmer 1725 X spectrometers, at room temperature. The polarised reflectance spectra for single crystals of $(BEDT\text{-}TTF)_2W_6O_{19}$ and $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ were studied in the frequency range 600 - 7000 cm^{-1} with a 1725 X spectrometer equipped with an IR microscope, a suitable polariser and a narrow-band MCT detector. An Oxford Instruments helium cryostat was used for measurements of the reflectivity of the crystals down to 4 K.

Results and discussion

According to Visentini et al.[9], two electronic bands are present at around 4500 and 7000 cm^{-1} in the dimerised salt of $(BEDT\text{-}TTF)_2Mo_6O_{19}$. The strong electronic band at 7000 cm^{-1} is associated with an intradimer charge transfer transition, but the medium 4500 cm^{-1} band with a lateral CT transition between dimers. The electronic absorption spectrum of isostructural salt $(BEDT\text{-}TTF)_2W_6O_{19}$ is similar to the salt mentioned above. The strong absorption band at ca. 6000 cm^{-1} and the weak band at ca. 4300 cm^{-1} are observed in the polarised transmission spectra recorded for a thin crystalline sample (Fig. 1). It is characteristic that the polarisations of both bands are perpendicular to each other; this corresponds well to electronic bands assignment proposed by Visentini et al.[9] In contrast, the spectrum of $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ is completely different. It consists of a strong band at about 11200 cm^{-1}, which can be attributed to the CT between cations.[12] Assuming that the nearest-neighbour Coulomb repulsion energies are small, the position of this band measures the on-side Coulomb repulsion between charges on the same BEDT-TTF molecule. The relatively weak band at about 7300 cm^{-1} originates from the CT between the neutral and ionic forms of BEDT-TTF. The differences in the electronic absorption spectra of $(BEDT\text{-}TTF)_2W_6O_{19}$ and $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ salts reflect the basic differences in their crystal structure and, as a result, their electrical transport properties (semiconductors in contrast to metal-like material).

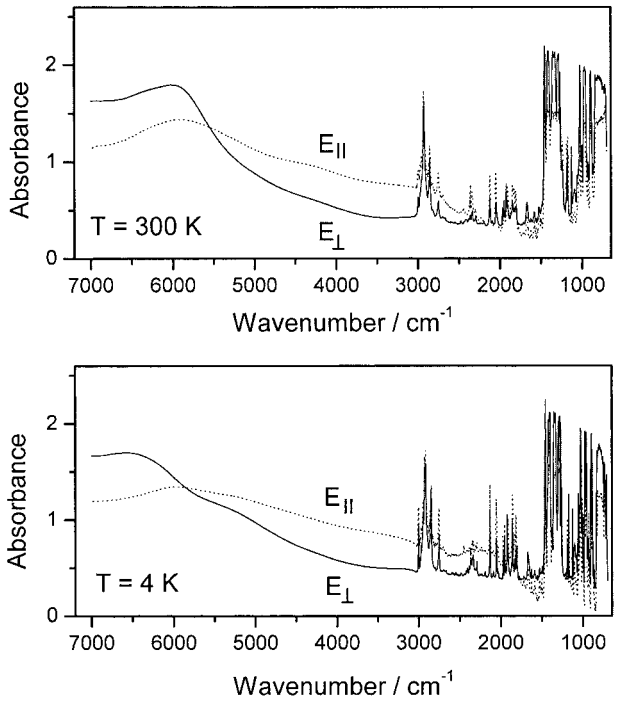

Figure 1. Anisotropy of the electronic and vibrational spectra of a $(BEDT\text{-}TTF)_2W_6O_{19}$ single crystal at 4 and 300 K.

Vibrational spectra of $(BEDT\text{-}TTF)_2W_6O_{19}$ were recorded in three ways: absorption of dispersed powdered sample in KBr matrixes, polarised/unpolarised transmission of thin single crystals and polarised reflection from a well developed face of the crystal. The anisotropy of the transmission spectra (Fig. 1) of a $(BEDT\text{-}TTF)_2W_6O_{19}$ crystal suggests that the electronic transition at about 6000 cm^{-1} occurs mainly along the BEDT-TTF step-chains (for perpendicular polarisation it is much weaker). On the other hand, the much weaker band at about 4300 cm^{-1} is assigned to a lateral CT transition between neighbouring BEDT-TTF species. Besides, the sensitivity of transmission measurements in thin crystalline samples is much higher than that of transmission measurements of absorption in KBr pellet. It is also seen from Figs. 1 and 2 that the region of vibrational modes is extremely rich. Studies of transmission of crystalline samples permit to record numerous very weak bands between 2291 and 1488 cm^{-1}, which are not seen in standard absorption spectra. It seems that they represent higher harmonic and/or combination modes of the BEDT-TTF cation. Vibrational features observed in $(BEDT\text{-}TTF)_2W_6O_{19}$ and $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ salts are reported in Table 1.

Table 1. Frequencies and assignments of infrared vibrational features of $(BEDT\text{-}TTF)_2W_6O_{19}$ and $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$.

Frequencies[a], cm^{-1}			Assignment[9-17]
$(BEDT\text{-}TTF)_2W_6O_{19}$ from KBr	$(BEDT\text{-}TTF)_2W_6O_{19}$ from single crystal	$(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ from KBr pellet	
2998 m	2995 m		
2972 m	2974 m		
2940 sh	2941 w		
2924 m	2926 m		
2850 vw	2853 w		
2820 vw	2817 w		
2742 vw	2747 m		
2690 vw	2693 vw		
2361 vw	2360 vw		
2337 vw	2333 vw		
	1454 m		
1452 m	1452 w	1451 m	$A_g(\nu_2)$
	1426 w		
1420 sh	1422 vs		
1415 vs	1419 vs	1416 vs	$A_g(\nu_3)$
	1410 sh		
1350 sh	1356 vw		
1343 vs	1344 vs	1341 vs	$A_g(\nu_3)$
1294 vw	1294 w	1293 sh	$B_{3g}(\nu_{57})$ or $B_{1u}(\nu_{29})$
1282 m	1284 m	1282 m	$A_g(\nu_5)$
	1260 vw	1257 vw	$B_{3u}(\nu_{67})$
	1238 vw		
	1185 vw		
1169 w	1174 vw	1169 w	$A_u(\nu_{1u})$
	1127 vw	1127 vw	$B_{1g}(\nu_{21})$
	1059 vw		
1025 w	1025 w	1027 m	$B_{3g}(\nu_{58})$
	1007 vw	1007 vw	$B_{3g}(\nu_{59})$
	993 vw		
974 s	977 w	976 s	W_6O_{19} and $A_g(\nu_6)$
962 s	963 w	963 s	Mo_8O_{26}, W_6O_{19}
	923 m	927 w	$A_g(\nu_7)$
	897 vw	896 w	$B_{2u}(\nu_{49})$
		884 w	$B_{3g}(\nu_{60})$
813 ms		814 sh	W_6O_{19}
803 vs		805 vs	Mo_8O_{26}, W_6O_{19}
		720 w	
		676 w	DMF
		669 w	DMF
		645 w	$A_g(\nu_8)$
585 m		585 m	W_6O_{19}
493 m		493 m	$A_g(\nu_9)$
478 m		478 m	$B_{1u}(\nu_{3u})$
444 s		443 s	W_6O_{19}, $A_g(\nu_{10})$
		406 w	DMF

[a] Intensities: vs – very strong, m – medium, w – weak, vw – very weak, sh – shoulder.

The IR spectra of both investigated salts contain several bands representing normal vibrations of species forming the compound: BEDT-TTF cations, $W_6O_{19}^{2-}$, $Mo_8O_{26}^{4-}$ anions and/or

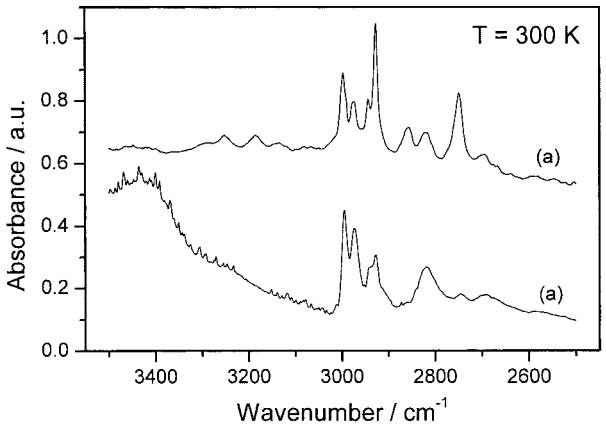

Figure 2. Infrared absorption spectrum of $(BEDT\text{-}TTF)_2W_6O_{19}$ (a) in KBr pellet, (b) transmission spectrum recorded for thin crystalline sample, at room temperature in the range of CH_2 vibrations.

solvent molecules. The strongest and broadest BEDT-TTF bands observed in transmission spectrum of $(BEDT\text{-}TTF)_2W_6O_{19}$ are given by its totally symmetric vibrations activated by the electron-molecular vibration (EMV) coupling: 1452 (ν_2), 1419 and 1344 (ν_3), 1284 (ν_5), and 923 cm^{-1} (ν_7). These activated bands are distinctly shifted relative to the corresponding Raman lines of BEDT-TTF molecules. There are also a few weaker bands representing active IR vibrations of BEDT-TTF species. Some bands originate from the vibrations of anionic ($W_6O_{19}^{2-}$ or $Mo_8O_{26}^{4-}$) sublattices. Few weak bands of $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ can be attributed to solvent vibrations. These bands are not distinctly shifted in comparison with the free solvent vibrations, suggesting weak interaction between DMF and the species forming the salt.

In order to properly analyse the structured bands of the $(BEDT\text{-}TTF)_2W_6O_{19}$, which dominate the IR spectra of the salt, they were decomposed and fitted at each temperature to Gaussian form by the least-square method (Fig. 3). An analysis of T-dependences of the component band frequencies, their bandwidths and integral intensities shows that nearly all bands shift (with no discontinuities) by a few cm^{-1} (0.5 – 0.01 %) towards higher frequencies with decreasing temperature. Usually, the bandwidth decreases distinctly (more than twice) and the integral intensity increases also without discontinuities by tens of % (Fig. 4). This is caused by shortening (strengthening) of molecular bonds in BEDT-TTF cations. Only the band at 1057 cm^{-1} undergoes an extreme intensity increase (more than 14 times). On the other hand, the 1127 cm^{-1} component shows a unique deviation from the above rules. Its frequency slightly decreases (more than 1 cm^{-1}) with temperature but the bandwidth decreases only by

about 7 %. This band is assigned to bending vibrations of CCH and SCH bonds of BEDT-TTF cation. A softening of the band is probably caused by stepwise hindering of the CH_2 motions. In contrast to this observation, some electronic parameters evaluated from a Drude-Lorentz analysis of the reflectance spectra of $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ salt show a temperature anomaly at about 180 K.[12] The features in the T-dependences of the plasma frequency and the relaxation rate correlate well with the electric conductivity properties reported elsewhere.[12]

The polarised reflectance spectra of $(BEDT\text{-}TTF)_2W_6O_{19}$ single crystals corresponding to two extreme polarisations at two selected temperatures (300 and 4 K), are reported in Fig. 5. The parallel polarization ($E_{||}$) has been found for the maximum of reflected energy along the long axis of the crystals. For the polarization perpendicular ($E_{\perp}$) to the above, the reflected energy reaches minimum. The spectra show an anisotropy for both electronic and vibrational excitations. For $E_{||}$ light polarization, the band at 6000 cm^{-1} as well as its vibrational features

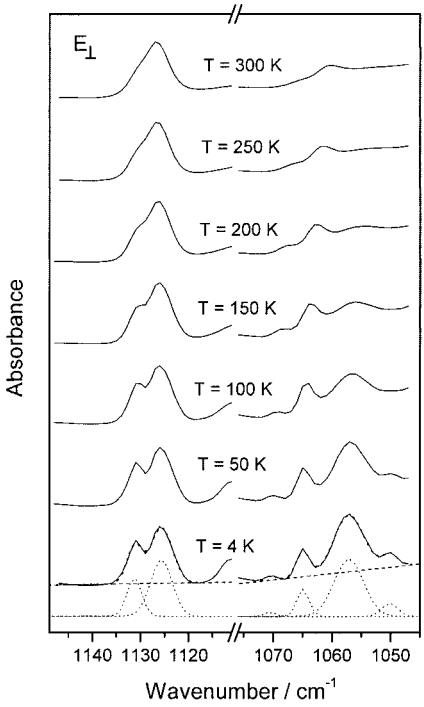

Figure 3. Temperature evolution of the bands in the region of stretching and bending vibrations of CH, SCH and CCH groups of BEDT-TTF. Dotted lines represent the best band decomposition.

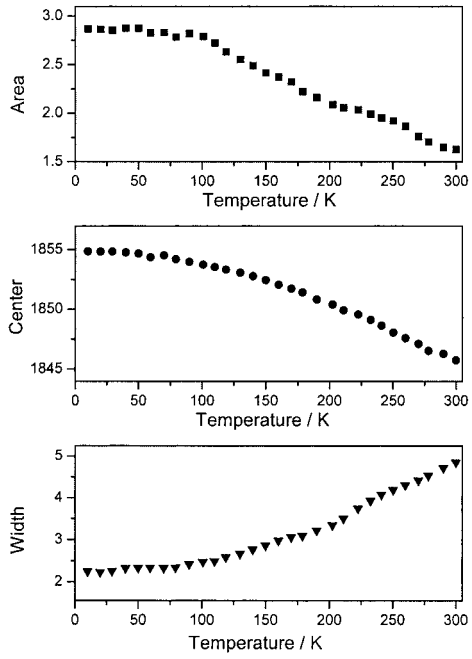

Figure 4. Temperature dependences of the frequency, bandwidth and integral intensity of the 1846 cm^{-1} component.

are relatively strong confirming the anisotropy of the crystal mentioned before. The vibronic structure is perfectly visible in both transmission (Fig. 1) and reflection (Fig. 5) spectra of

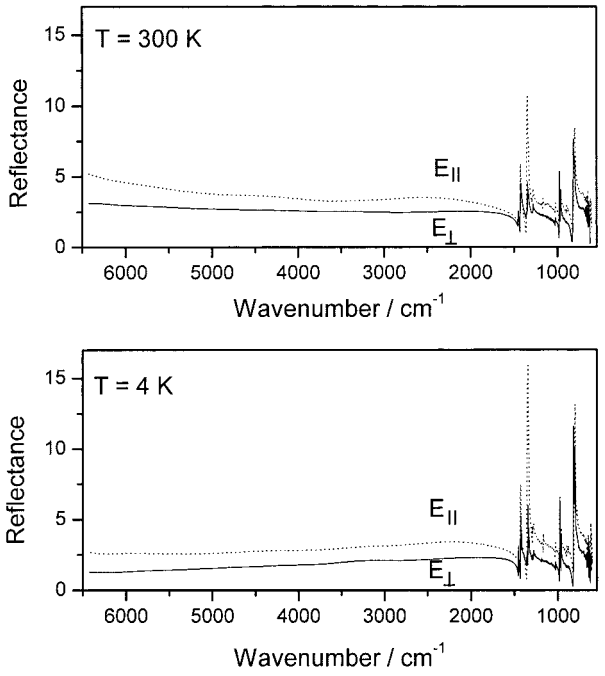

Figure 5. Polarised reflectance spectra of $(BEDT\text{-}TTF)_2W_6O_{19}$ single crystals at $T = 300$ K and at $T = 4$ K for parallel and perpendicular polarizations of the IR beam.

$(BEDT\text{-}TTF)_2W_6O_{19}$ crystals. The occurrence of developed vibronic features in the IR spectra is typical of organic semiconductors. On the contrary, metallic properties of $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$ salt are confirmed by poorly visible structure in the spectra below 1500 cm^{-1}.[12] Its spectral anisotropy is much greater than that reported previously for the semiconducting $(BEDT\text{-}TTF)_2W_6O_{19}$ salt. The anisotropy of the salt is adequate to its layered structure and metallic properties well fitted by the Drude-Lorentz dielectric function for $E_\perp$ light polarisation.

The optical conductivity spectra $\sigma(\omega)$ of $(BEDT\text{-}TTF)_2W_6O_{19}$ were obtained by the Kramers-Krönig transformation of their reflectivity (Fig. 6). It was performed in the range 600-6500 cm^{-1} by extrapolating the reflectance data to zero frequency with a constant value. For the extrapolation to higher frequencies, we used experimental data for $(BEDT\text{-}TTF)_2Mo_6O_{19}$.[9] The conductivity spectra of $(BEDT\text{-}TTF)_2W_6O_{19}$ show a distinct vibronic structure below 1500 cm^{-1}. This structure is the consequence of strong coupling of totally symmetric A_g

vibrations of the BEDT-TTF^{+} cation to suitable electronic excitations. The intensity of vibronic bands increases strongly at low temperature. The $\sigma(\omega)$ spectra of the (BEDT-TTF)$_6$(Mo$_8$O$_{26}$)(DMF)$_3$ salt do not change with temperature and they are qualitatively similar above 2000 cm^{-1}, for a given polarization. For $E_{||}$ polarization, the intensity of the large vibronic band at about 1300 cm^{-1} increases considerably at 4 K. This band is mainly a consequence of strong coupling of totally symmetric A_g vibrations of C=C bonds with intrastack or interstack charge transfer. For the neutral BEDT-TTF molecule, the two A_g modes observed at $A_g(\nu_3) = 1493$ cm^{-1} and $A_g(\nu_2) = 1551$ cm^{-1} are assigned to C=C stretching.[15] Due to the strong vibrational coupling of these modes, a single, intense and broad vibrational feature is usually observed in salts with partially ionised BEDT-TTF molecules. The situation is completely different for $E_{\perp}$ polarization, which reveals metal-like properties of the (BEDT-TTF)$_6$(Mo$_8$O$_{26}$)(DMF)$_3$ salt. At room temperature, a strong interband transition is observed at about 2400 cm^{-1}. On the low-frequency wing, a strong and structured band corresponding to vibronic effects is also seen. At about 1500 cm^{-1}, typical antiresonance

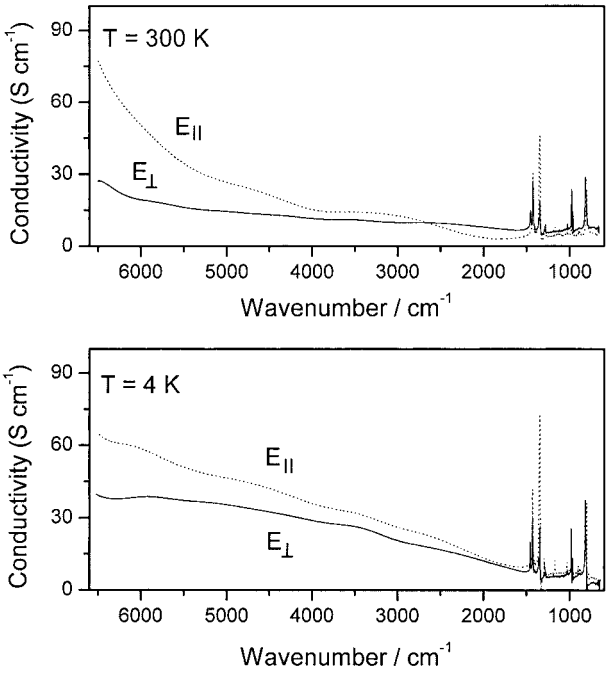

Figure 6. Optical conductivity spectra of (BEDT-TTF)$_2$W$_6$O$_{19}$ as obtained by the Kramers Krönig analysis of the reflectance spectra for parallel and perpendicular polarizations at $T = 4$ K and $T = 300$ K.

is observed, which results from a coupling between the intramolecular vibrations and the interband electronic transition.

Conclusion

The semiconducting $(BEDT\text{-}TTF)_2W_6O_{19}$ salt, single crystals and powdered samples, was investigated in a broad spectral range at various temperatures. The salt shows similarities to $(BEDT\text{-}TTF)_2Mo_6O_{19}$ but is completely different from the metal-like $(BEDT\text{-}TTF)_6(Mo_8O_{26})(DMF)_3$. The electronic absorption spectrum of the salt under study consists of two bands at about 6000 and 4300 cm^{-1} showing anisotropy. The vibrational spectrum of $(BEDT\text{-}TTF)_2Mo_6O_{19}$ is dominated by totally symmetric modes of the cation activated by electron-molecular vibration coupling. The spectra recorded for thin single crystals of the salt are very rich and contain several very weak bands, which could be attributed to harmonic and/or combination modes of the $BEDT\text{-}TTF^+$ cation.

Acknowledgements

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