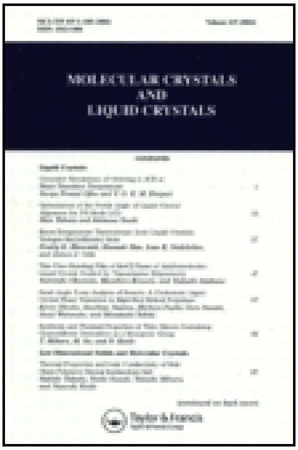

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Mixtures of Trihalide Anions in Isostructural BEDT-TTF Salts as Seen by Raman Spectroscopy

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Low frequency Raman spectra have been recorded at room temperature for β-type structure of the $(BEDT\text{-}TTF)_2X$ single crystals (where BEDT-TTF is bis(ethylenedithio) tetrathiafulvalene and X stands for mono or mixed trihalide anions). This technique has permitted us to detect a presence of the $(Br\text{-}I\text{-}Cl)^-$, $(I\text{-}I\text{-}Cl)^-$and $(Cl\text{-}I\text{-}Cl)^-$ anions in addition to a mixture of the $(I\text{-}I\text{-}I)^-$, $(I\text{-}I\text{-}Br)^-$ and $(Br\text{-}I\text{-}Br)^-$ anions in some recently grown single crystals. The observed low-frequency Raman bands were compared with the *ab initio* calculated vibrational frequencies of trihalide anions and a very good agreement between experimental and calculated data was found.

Keywords: Raman spectroscopy; BEDT-TTF; organic conductors and superconductors; *ab initio* calculations

INTRODUCTION

Charge-transfer salts based on BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] radical cation donor yield a great variety of organic conductors [1–6]. The nature of intermolecular interactions leading to superconductivity in some of these systems is not yet entirely understood, however it has been found to depend on the chemistry of anions [6–8]. Raman spectroscopy has proven to be an efficient tool for studying the BEDT-TTF trihalide organic conductors [9–12], moreover it was also successfully applied to observation of individual contributions of specific

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trihalide anions in mixed structures [13–15]. The content of halide atoms is commonly determined on a basis of X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). These techniques give only a quantitative trihalide anion composition. Recently performed Raman experiments confirmed the existence of a ternary mixture of I_3^-, I_2Br^- and IBr_2^- anions in the crystal structure of β-(BEDT-TTF)$I_{1.5}Br_{1.5}$ salt [13,15] and a ternary mixture of IBr_2^-, $BrICl^-$ and ICl_2^- anions in the β"-(BEDT-TTF)$Br_{0.5}ICl_{1.5}$ single crystals [14,15]. In was shown [15] that quantum mechanics *ab initio* self-consistent field methods are useful for the proper assignment of experimental frequency vibrations in salts containing mixture of trihalide anions. These results of Raman investigations gave rise to further investigation, that have consisted in crystallization and characterization of physical properties (*i.e.* electrical and optical) of new single crystals of BEDT-TTF with mixture of trihalide anions.

In this work we present a Raman investigations of isostructural β-(BEDT-TTF)$_2$X organic conductors containing mixture of three and more different trihalide anions. The β-type structure of such crystalline compounds corresponds to triclinic ($P\overline{1}$) space group where BEDT-TTF radical cations form organic layers alternating with those of trihalide anions along the crystallographic *c*-axis. Trihalide anions are aligned approximately along the *[110]* direction and BEDT-TTF radical cations form quasi-2D conductive layers in the *(001)* plane [1–4]. Until now all known BEDT-TTF trihalide salts forming β-type structure contain trihalide anions based on iodine and bromide [1–8], while those containing in addition chloride atoms exhibit rather β'-or β"-type structures [16].

EXPERIMENTAL

Single crystals of β-(BEDT-TTF)$_2$X, where X stands for I_3, IBr_2, or quantitatively $I_{2.85}Br_{0.15}$, $I_{1.5}Br_{1.5}$, $I_{2.3}Cl_{0.7}$, $Br_{1.3}I_{1.2}Cl_{0.4}$ and $Br_{0.8}I_{1.6}Cl_{0.6}$ were prepared by chemical oxidation method [17] in nitrobenzene under argon atmosphere. The β-type crystal structure was confirmed based on election spin resonance (ESR) and XRD measurements. The halide compositions were obtained by EDX.

Raman experiments

The Raman spectra of single crystals were recorded at room temperature using a Jobin-Yvon T64000 Micro-Raman spectrometer working in back-scattering mode. The measurements were performed with spectral resolution of 2 cm^{-1}

using 632 nm He-Ne (Spectra Physics model 127) laser line. The laser beam power was kept below 0.1 mW with an illuminated spot of about 8 μm in diameter, giving an energy density of 400 kW/m^2. Diamond (1332 cm^{-1}) and silicon (520 cm^{-1}) lines were used for the calibration of the spectrometer. For all the investigated crystals, the Raman spectra were recorded at the *(001)* crystallographic plane, and the laser light was linearly polarized approximately along the long axis of trihalide anions *i.e.* approximately along *[110]* direction.

Ab initio calculations

Ab initio calculations of trihalide anions vibrational frequencies have been performed using GAMESS Version 18.03.1997. The self-consistent field (SCF) procedure was carried out for the restricted Hartree-Fock (RHF) method. The LCAO molecular orbital was constructed for the basis set based on effective core potential (ECP) Stevens/Basch /Krauss/Jasien/Cundari (SBK) for Li-Rn with diffusion and polarization functions (three for p and d orbitals, and one for f orbitals). All calculations were performed for free I_3, I-I-Br, Br-I-Br, Br-I-Cl, I-I-Cl and Cl-I-Cl one-negatively charged anions (without an external potential). The vibrational frequencies were calculated by numerical diagonalization of the obtained density matrix.

RESULTS AND DISCUSSION

The results of the quantum-chemical *ab initio* calculations of vibrational modes for trihalide anions are given in Table I. We decided to compare frequencies of vibrational modes calculated by GAMESS for free anions with the experimental ones. It is reasonable since the bond lengths calculated by GAMESS for free anions are similar to those obtained experimentally while the *ab-initio* calculations for trihalide anions in crystal structure are much more difficult.

The Raman spectrum of β-(BEDT-TTF)$_2$I$_3$ single crystal (Fig. 1a) is composed of bands at 24, 28, 95, 120, 144 and 241 cm^{-1}. The first two bands are lattice modes, the 120 cm^{-1} band was assigned to the Raman active in-phase stretch of symmetrical linear I_3^- anions, while the weak band at 95, 144 and 241 cm^{-1}was recognized as overtones [9–12]. The recorded spectrum is relatively intense due to resonant enhancement of the Raman scattering by I_3^- anions.

The similar Raman spectrum characterizes the β-(BEDT-TTF)$_2$I$_{2.85}$Br$_{0.15}$ single crystals (Fig. 1b). Two bands at 120 and 241 cm^{-1} are exactly at the same positions as that for the β-(BEDT-TTF)$_2$I$_3$ single crystals, indicating the presence of I_3^- ani-

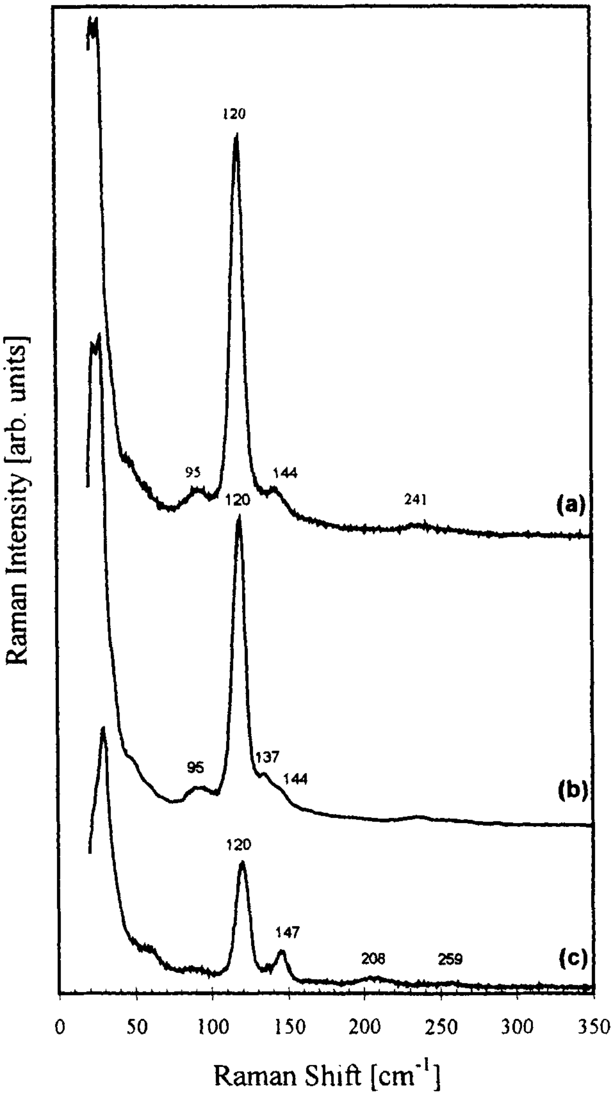

FIGURE 1 The Raman spectra of β-(BEDT-TTF)$_2$I$_3$(a), β-(BEDT-TTF)$_2$I$_{2.85}$Br$_{0.15}$(b) and β-(BEDT-TTF)$_2$I$_{2.3}$Cl$_{0.7}$ (c) salts taken at room temperature for 632.8 nm laser line polarised along trihalide anion's long axis

ons. The band at 187 cm^{-1} is expected to result from the presence of non-symmetrical linear I$_2$Br$^-$ anions and we assign it to the in-phase-stretching mode (Table I).

Quite different spectrum was obtained for the β-$(BEDT\text{-}TTF)_2I_{2.3}Cl_{0.7}$, where the bands at 28, 120, 147, 208 and 259 cm^{-1} were found (Fig. 1c). The overtones at 95 and 144 cm^{-1} are less intense in comparison to the previous spectra, probably due to disappearance of the band at 24 cm^{-1}. The band at 147 cm^{-1} can be explained as normally Raman inactive out-of-phase stretching of I_3^-, $I_2C_l^-$ or ICl_2^- anions [9–12], while 208 and 259 cm^{-1} bands are probably due to $I_2Cl^-$and ICl_2^- anions [14–16], respectively (Table I).

TABLE I Experimental bond distances and in-phase vibrations frequencies of I_3, I_2Br, IBr_2, IClBr and ICl_2 anions in BEDT-TTF salts and *ab initio* calculated values for free I_3, I_2Br IBr_2, IClBr, I_2Cl and ICl_2 anions [15]

Salt/anion type	*Bond length (Å)*	*In-phase stretch [cm^{-1}]*
(I-I-I)$^-$	2.919^a	120^a
	2.96^b	117.8^b
(I-I-Br)$^-$	2.92/2.70^a	136^a
	2.95/2.75^b	145.7^b
(Br-I-Br)$^-$	2.704^a	160^a
	2.74^b	163.6^b
(Cl-I-Br)$^-$	-	230^a
	2.59/2.74^b	233.6^b
(Cl-I-Cl)$^-$	-	259^a
	2.59^b	266.5^b
(I-I-Cl)$^-$	-	208^a
	2.95/2.60^b	223.7^b

a. Experimental data from XRD [2–6] and Raman [9–15].
b. *Ab initio* calculated data (GAMESS) [15].

Figure 2 shows the Raman spectra of other β-type BEDT-TTF trihalide single crystals. Fig. 2a presents the well-known Raman spectrum of β-$(BEDT\text{-}TTF)_2IBr_2$ single crystal. Independently on the crystal lattice modes below 70 cm^{-1}, that are common for all presented in Fig. 2 spectra, one can see 136 and 160 cm^{-1} bands. The former is probably due to small amount of I_2Br^- anions and the latter is due to IBr_2^- anions [10,16] (Table I). In the Raman spectrum of β-$(BEDT\text{-}TTF)_2I_{1.5}Br_{1.5}$ single crystal (Fig. 2b) there are three bands at about 120, 136 and 160, that were attributed to I_3^-, $I_2Br^-$and IBr_2^- anions respectively (Table I). This salt was the first one in which the existence of ternary mixture of trihalide anion was proven by Raman spectroscopy [13,15].

Fig. 2c shows the Raman spectrum of the β-$(BEDT\text{-}TTF)_2Br_{1.3}I_{1.3}Cl_{0.4}$. There are four main bands over 100 cm^{-1} frequency. Similarly like for the previous

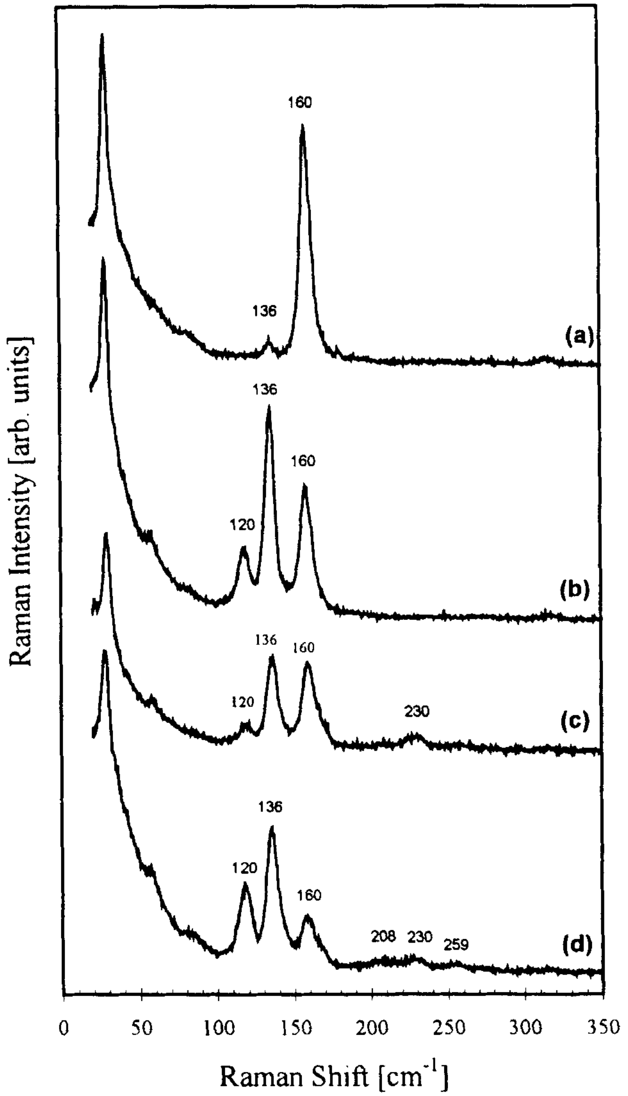

FIGURE 2 The Raman spectra of β-(BEDT-TTF)$_2$IBr$_2$(a), β-(BEDT-TTF)$_2$I$_{1.5}$Br$_{1.5}$(b), β-(BEDT-TTF)$_2$Br$_{1.3}$I$_{1.3}$Cl$_{0.4}$ (c) and β-(BEDT-TTF)$_2$Br$_{0.8}$I$_{1.6}$Cl$_{0.6}$ (d) salts taken at room temperature for 632.8 nm laser line polarised along trihalide anion's long axis

salt, there are three bands at 120, 136 and 160 cm^{-1} corresponding to I$_3^-$, I$_2$Br$^-$ and IBr$_2^-$ anions, but additionally a new band at 230 cm^{-1} is observed. We attribute it to non-symmetrical linear BrICl$^-$ anion (Table I). Since bromine atoms are in majority and few chlorine atoms are included in the structure the formation of the I_2Cl^- or ICl_2^- anions is much less probable than of the $BrICl^-$ anions. The band at about 230 cm^{-1} has been already observed for the β"-$(BEDT\text{-}TTF)_2Br_{0.5}ICl_{1.5}$ single crystals and it was attributed to the $BrICl^-$anions [15]. According to the Raman spectroscopy data the β-$(BEDT\text{-}TTF)_2Br_{1.3}I_{1.3}Cl_{0.4}$ single crystal consists of mixture of four trihalide anions – I_3^-, I_2Br^-, IBr_2^- and $BrICl^-$, and among them the IBr_2^- anions occur in majority.

Another single crystal possessing β-type structure was assigned using the EDX measurements as β-$(BEDT\text{-}TTF)_2Br_{0.8}I_{1.6}Cl_{0.6}$. In the Fig. 2d one can see that its Raman spectrum consists of six bands above 100 cm^{-1}. By using the *ab initio* calculated in-phase stretching modes (Table I) all the observed bands can be attributed to specific trihalide anions. The bands at 120, 136, 160, 208, 230 and 259 correspond to I_3^-, I_2Br^-, IBr_2^-, I_2Cl^-, $BrICl^-$ and ICl_2^- anions, respectively. By taking the Raman spectra of β-$(BEDT\text{-}TTF)_2Br_{0.8}I_{1.6}Cl_{0.6}$ single crystal we have found that apart the mixture of bigger trihalide anion also smaller trihalide anions like I_2Cl^- and ICl_2^- can be incorporated into the β-type structure of BEDT-TTF trihalides. This can happen if amount of chlorine atoms is small enough, otherwise β′ or β"-type structures will be formed [16].

CONCLUSION

By using Raman spectroscopy we have demonstrated that the composition of trihalide anions in the β-$(BEDT\text{-}TTF)_2X$ single crystal can be rather complicated. We have found that binary mixture of halide atoms, iodine with chlorine and iodine with bromine result in ternary mixtures of trihalide anions. The more complicated ternary mixture of I, Br and Cl atoms may result in mixture of many trihalide anions.

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