Temperature and Pressure Dependence of the Crystal Structure of the Magnetic Molecular Conductor: (BEDT-TTF)₃CuBr₄

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Abstract. — The magnetic molecular semiconductor (BEDT-TTF)₃CuBr₄ (BEDT-TTF: bis(ethylenedithio)-tetrathiafulvalene) exhibits a phase transition at 60 K accompanied by an abrupt fall in magnetic susceptibility. It also shows the largest increase of conductivity with pressure of all organic conductors with a transition to a metallic state at about 5 kbar. The temperature dependent structural study (10 – 298 K) shows that the positive charge localised on one of the two crystallographically independent BEDT-TTF at room temperature is equally distributed at 10 K and furthermore that the CuBr₄²⁻ remains square planar, contrary to the hypothesis of a Jahn-Teller distortion suggested by EPR. The pressure dependent crystallographic study (0 – 15 kbar) may explain the dramatic effect of applying pressure on organic crystals. The intermolecular empty spaces are strongly reduced at 10 kbar explaining the increase of conductivity. The crystallographic results require the physical properties of this salt at low temperature to be re-examined.

Résumé. — Le sel (BEDT-TTF)₃CuBr₄ (BEDT-TTF: bis(éthylènedithio)-tétrathiofulvalène) présente une transition entre deux états semi-conducteurs qui s'accompagne d'une perte de susceptibilité magnétique à 60 K. L'application d'une pression engendre l'augmentation de conductivité la plus importante observée dans les conducteurs organiques et induit une transition vers un état métallique à 5 kbar. L'étude structurale en température (10 – 295 K) montre que la localisation de la charge sur l'un des deux cations cristallographiquement indépendants présente à température ambiante disparaît à 10 K et prouve que l'anion CuBr₄²⁻ reste de géométrie plan carré contrairement à ce qu'une distorsion de type Jahn-Teller suggérée par RPE pouvait laisser penser. L'étude structurale à haute pression (0–15 kbar) confirme que le caractère monocristallin des cristaux organiques peut disparaître par application de pression. Les espaces intermoléculaires sont considérablement réduits à 10 kbar en accord avec l'évolution de la conductivité. Au regard de ces résultats, les propriétés physiques de ce sel paraissent devoir être réexaminées.

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1. Introduction

Although charge transfer salts of BEDT-TTF {bis(ethylenedithio)-tetrathiafulvalene} have been investigated intensively for the last fifteen years, novel and unusual properties are still coming to light. For example there has been a lot of interest in the interplay between magnetism and conductivity with the recent report of the first BEDT-TTF salt with a magnetic anion to become superconducting [1]. The two hundred BEDT-TTF salts which have been synthesised up to now exhibit very different structural and physical properties, largely as a result of the association of the BEDT-TTF donor with many different anions. Indeed, much effort has been devoted to attempt to understand and control the structural arrangement and hence the properties of these salts, so far with little success.

The novelty of the BEDT-TTF salts comes essentially from the planarity of the donor molecule and its capacity for developing S-S contacts between neighbours. Hence BEDT-TTF salts are often two dimensional from the conductivity point of view. Another feature is the frequent occurrence of strong disorder at the extremities of the BEDT-TTF under ambient conditions. Furthermore, in a number of cases, one observes that charge is localised differentially on different BEDT-TTF molecules in the same salt.

BEDT-TTF salts often undergo transitions by lowering the temperature (*e.g.* from metallic to insulating) that can be suppressed by applying pressure and in many cases the suppression of this kind of transition leads to a superconducting state, so that more than fifty BEDT-TTF salts have been reported as superconductors at very low temperature under pressure or at ambient pressure. So, for all these reasons, it is important to gain access to detailed information about the structural properties at very low temperatures and high pressures. For technical reasons, complete structural studies under such conditions are very rare, but in the present paper we describe a crystallographic investigation of the $(\text{BEDT-TTF})_3\text{CuBr}_4$ at high pressure and low temperature.

The physical properties of this salt have been reported [2] as well as its structural arrangement under ambient conditions [3]. $(\text{BEDT-TTF})_3\text{CuBr}_4$ is a semiconductor at ambient pressure and undergoes a transition between two semiconducting states at 50-60 K, the activation energy being higher at high temperature than below the transition. Applying pressure has a dramatic effect on the conductivity, increasing by a factor of 500 from 1 bar to 20 kbar, so that it becomes metallic at around 5 kbar. The thermopower is consistent with a Mott-Hubbard behaviour at ambient pressure. The optical properties indicate that one BEDT-TTF cation carries a charge close to one while the other remains approximately neutral. The magnetic susceptibility decreases abruptly between 50 and 60 K probably as a result of the loss of the cation contributions. The g values suggest that the CuBr_4^{2-} adopts a square planar conformation at ambient temperature and pressure and a distorted tetrahedral one below 60 K. The $(\text{BEDT-TTF})_3\text{CuCl}_2\text{Br}_2$ salt is isostructural [4] and its physical properties are very similar.

In order to understand these remarkable changes in physical behaviour we have determined the crystal structure of $(\text{BEDT-TTF})_3\text{CuBr}_4$ as a function of temperature (298 – 10 K) and pressure (1 bar - 15 kbar). Figure 1 shows a schematic phase diagram with the range of the crystallographic investigations.

2. Experimental

The crystals of $(\text{BEDT-TTF})_3\text{CuBr}_4$, prepared as described previously, are thin black needles (~ 0.01 mm) elongated along the b -axis. The quality of each crystal was checked by X-ray diffraction on film before use.

Fig. 1. — Schematic phase diagram of ET_3CuBr_4 , data collection points (circles) and range of crystallographic studies (dashed lines).

2.1. HIGH PRESSURE STUDY. — Single crystal crystallographic studies on conducting organic materials at high pressures are very rare because of the experimental difficulties and the softness of the crystals. To our knowledge, only eight such studies have been reported (see Tab. VI), six with diamond anvil cells with a beryllium gasket (Bridgmann type), one with a diamond anvil cell (Merill-Basset type) and two with a gas pressure cell.

For the present study we used a Bridgmann cell [5] with a high pressure cavity 0.35 mm diameter and 0.30 mm high. The pressure is measured from the variation of the wavelength of maximum absorption of a thin film of $\text{Ni}(\text{DMG})_2$ (DMG = dimethylglyoxime) [5]. The accuracy for the measured pressure is estimated to be ± 0.3 kbar. The pressure inside the cell was monitored before and after each measurement at a given pressure.

The diffracted intensities from a crystal at 4.5 kbar and 10 kbar were recorded on a two circle STOE diffractometer (see Tab. I). The profile of each reflection was examined visually and the integrated intensity calculated. The volume of the crystal was very small ($4 \times 10^{-4} \text{ mm}^3$) resulting in very weak reflections and the small number of reflections used in the structural refinement. The refinement was performed using the program ORION [6], starting with the atomic coordinates found at ambient temperature and pressure [3]. Because of the small number of observed reflections, we used blocks composed of each entity (BEDT-TTF and CuBr_4^{2-}) of the asymmetric unit. Thus only the center of gravity of the BEDT-TTF and CuBr_4 were refined at high pressure.

Data for the cell parameters were obtained on a three circle Hüber diffractometer from 1 bar to 13.5 kbar. Above 13.5 kbar, the reflections become broad and less detectable. The initial closing of the cell in a fluorinert bath resulted in a pressure of 1.2 kbar that gradually increases to 2.5 kbar in around ten hours. So, no good results have been obtained from 1 bar to 2.5 kbar.

No superstructure reflections were observed at 4.5, 6.3, 13.5 and 15 kbar on films obtained using a Weissenberg camera, though the weakness of the spots only allowed us to observe the most intense Bragg reflections.

2.2. LOW TEMPERATURE STUDY. — After several attempts at collecting data at low temperatures we realised that the crystals do not resist thermal cycling. It is not clear whether the rate of cooling or the possible twinning of the crystals were responsible of the non-reversibility.

Table I. — *Experimental and crystallographic data for the study ET_3CuBr_4 at high pressure and low temperature. (* Refinement based on the center of gravity of each molecule, ** refinement based on the atomic coordinate).*

Temperature	295 K	295 K	130 K	10 K
Pressure	4.5 kbar	10 kbar	1 bar	1 bar
Crystal dimension	$0.13 \times 0.10 \times 0.01$	$0.13 \times 0.10 \times 0.01$	$0.80 \times 0.25 \times 0.03$	$2.00 \times 0.25 \times 0.03$
Diffractometer	Stoe 2 circles	Stoe 2 circles	Nonius 4 circles	Huber 3 circles
System	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	16.909(12)	16.796(13)	16.958(6)	16.905(24)
b (Å)	10.053(16)	9.960(17)	10.074(2)	10.101(32)
c (Å)	13.935(11)	13.664(12)	14.038(7)	13.909(21)
β (Å ³)	102.31(3)	101.35(3)	102.61(4)	102.47(4)
V (Å ³)	2314(7)	2237(8)	2340(3)	2319(15)
Absorption correction	no	no	yes	yes
Criterion	$I/\sigma(I) > 3^*$	$I/\sigma(I) > 3^*$	$I/\sigma(I) > 3^{**}$	$I/\sigma(I) > 3^{**}$
Reflection measured	6411	6534	4064	4439
After profiles examination	2950	3016	-	-
Independent	2112	2203	2062	3566
Observed	728	460	1623	2806
Used in refinement	631	392	1602	2779
R_{int} (%)	4.6	4.8	3.6	3.1
R	7.7*	7.6*	5.3**	5.0**
R_w	5.8*	6.0*	5.4**	4.3**

The crystals appear to have little fractures which may be deduced from close examination of Weissenberg films; lowering temperature enhances these fractures. We verified that these deformations can be attributed to the crystal quality and not to structural changes.

Weissenberg photographs were recorded with Cu $K\alpha$ radiation at several temperatures on cooling slowly from 295 to 10 K. We then collected two sets of intensities, one at 130 K on a four circle Nonius diffractometer equipped with a cold nitrogen flow and the other at 10 K on a three circle Hüder diffractometer equipped with a closed cycle helium refrigerator [5, 7]. The structure was solved in both cases using the program ORION. We proceed first by finding the center of gravity of each molecule as in the high pressure refinement and then refining all the parameters of each atom (see results in Tab. I). The temperature dependence of the cell parameters was measured on the four circle diffractometer on warming from 100 to 298 K. We add to this list those obtained on the three circle diffractometer at 10 K.

Fig. 2. — View of a conducting sheet along the intramolecular axis of the entity A of ET_3CuBr_4 .

3. Crystal Structure of $(\text{BEDT-TTF})_3\text{CuBr}_4$ at High Pressure and Low Temperature

3.1. $(\text{BEDT-TTF})_3\text{CuBr}_2\text{Y}_2$ ($\text{Y} = \text{Cl}$ OR Br). — $(\text{BEDT-TTF})_3\text{CuBr}_4$ and $(\text{BEDT-TTF})_3\text{CuCl}_2\text{Br}_2$ are isostructural. They belong to the monoclinic space group $\text{P}2_1/\text{c}$; the asymmetric unit contains one BEDT-TTF cation on a general position (labelled A), one neutral BEDT-TTF on a centre of inversion (labelled B) and half the copper atom and two bromine atoms. The copper atom is also on a centre of inversion. In the mixed halide salt the halogens are not distinguishable.

The structural arrangement consists of alternate layers of the organic molecules and the copper halide anions. Within the organic layers, the molecules are stacked along the c axis with $\text{S} \cdots \text{S}$ interactions along b (Fig. 2). Each stack contains the sequence $\cdots\text{AABAAB}\cdots$, the resulting plane being a slightly distorted honeycomb with the A molecules at the apex of the hexagons and the B molecules in the centres. This is reminiscent of the structure of $(\text{BEDT-TTF})_4[\text{KFe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$, where in this case there is a pair of BEDT-TTF $^+$ in the center of a hexagon made up of neutral BEDT-TTF molecules. The packing motif is the one that is described as the α -phase. The dihedral angle between the mean plane defined by the A molecules of adjacent stacks is $67.09(4)^\circ$.

At low temperature and high pressure, the crystals of $(\text{BEDT-TTF})_3\text{CuBr}_4$ belong to the same space group and display the same packing motifs; the main difference is the equivalence of the charge of the A and B molecules at low temperature.

3.2. VARIATION OF THE OVERLAP MODES. — Within each stack there are two kinds of overlap mode (Fig. 3); labelled a_1 between two A molecules and a_2 between A and B. In both cases the angle between the projection of the molecular axes on the mean plane is zero. The parameters defining the relative positions are given Table II where d is the interplanar separation, and Δx and Δy are the shifts along the short and long axes of BEDT-TTF. The a_1 mode is characterised by an intermolecular distance ($3.79 \text{ \AA}$) larger than the sum of van der Waals radii of the sulfur atoms. This distance decreases marginally under pressure but remains large at 10 kbar and at 10 K. For example it may be compared with the corresponding values of 3.66 and $3.48 \text{ \AA}$ for $\alpha'-(\text{BEDT-TTF})_2\text{X}$ at this pressure [8,9] or to $3.42 \text{ \AA}$ for $(\text{BEDT-TTF})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ at 10 K. In both cases, as for other α -phase salts, there is a large shift along the short axis of the molecules. We note that the difference between the two averaged distances is less at

Fig. 3. — Two packing motifs adopted by the molecules in ET_3CuBr_4 .

Table II. — Pressure and temperature dependence of the parameters defining the mode of overlap in ET_3CuBr_4 .

Overlap modes		ET_3CuBr_4				
		298 K	130 K	10 K	298 K	298 K
		1 bar	1 bar	1 bar	4.5 kbar	10 kbar
A-A ($1-x, -y, 1-z$): a_1	d (Å)	3.79	3.75	3.66	3.74	3.68
	Δx (Å)	3.29	3.23	3.29	3.22	3.10
	Δy (Å)	3.36	3.49	3.36	3.39	3.41
A-B ($x, 0.5-y, -0.5+z$): a_2	d (Å)	3.66	3.62	3.62	3.57	3.53
	Δx (Å)	2.42	2.37	2.29	2.36	2.27
	Δy (Å)	0.05	0.11	0.10	0.10	0.11

10 K (0.04 Å) than under ambient conditions (0.13 Å) or high pressure (0.15 Å) implying more regular chains at low temperature.

The intrastack interactions appear very weak whatever the temperature or pressure. They recall the overlap amplitudes encountered in $(\text{BEDT-TTF})_3\text{CuCl}_4 \cdot \text{H}_2\text{O}$ [9].

3.3. VARIATION OF THE INTERCHAIN INTERACTIONS. — Figure 4 shows the labelling of the interactions within a BEDT-TTF layer. Four different interactions between A and B are defined by seven short $\text{S} \cdots \text{S}$ contacts. Table III gives the shortest and the average of these distances. They are shorter than the intrastack $\text{S} \cdots \text{S}$ contacts and decrease strongly under constraint. The variation is continuous, the values at 130 K and 4.5 kbar being respectively intermediate between those obtained at 298 K and 10 K and those obtained at 1 bar and 10 kbar. The strongly increasing contact between stacks (**b** axis) under pressure is consistent with the increase in conductivity with pressure.

The dihedral angle between the averaged planes of BEDT-TTF from adjacent stacks ($67.09(4)^\circ$) decreases under constraint, being smaller at 10 K ($65.79(6)^\circ$) than at 4.5 kbar (67.0°) and even than at 10 kbar (66.2°).

3.4. THE ANION-CATION CONTACTS

3.4.1. The Anionic Network. — The volume occupied by the anion in $(\text{BEDT-TTF})_3\text{CuBr}_4$ (310 Å^3) is bigger than in $(\text{BEDT-TTF})_3\text{CuCl}_2\text{Br}_2$ (250 Å^3) or $(\text{BEDT-TTF})_3\text{CuCl}_4 \cdot \text{H}_2\text{O}$ (210 Å^3). The anions are planar and arranged in isosceles triangles with two short Cu-Cu distances of 8.715 Å and one long Cu-Cu distance of 10.14 Å . The two Br-Br distances are 4.183

Fig. 4. — Labelling of the interactions within a conducting sheet of ET₃CuBr₄.

Table III. — Pressure and temperature dependence of interstack intermolecular S-S contacts (Å) (*b*, *c*, *d* and *e* are defined in Fig. 4).

Temperature	298 K	130 K	10 K	298 K	298 K
Pressure	1 bar	1 bar	1 bar	4.5 kbar	10 kbar
Standard deviations	0.002	0.009	0.003	-	-
A-B. <i>d</i>					
Shortest S-S	3.532	3.461	3.448	3.442	3.359
average	3.832	3.809	3.775	3.764	3.693
A-A <i>c</i>					
Shortest S-S	3.361	3.331	3.307	3.322	3.268
average	3.578	3.533	3.504	3.515	3.450
A-B <i>b</i>					
Shortest S-S	3.537	3.495	3.462	3.484	3.339
average	3.724	3.687	3.652	3.636	3.597
A-A <i>e</i>					
Shortest S-S	3.362	3.328	3.306	3.322	3.268
average	3.578	3.532	3.503	3.514	3.451

and 7.0 Å. The anions become closer as the temperature is lowered or the pressure increased. The shorter Cu-Cu and Br-Br distances, 8.595 Å and 4.047 Å at 10 K, are very close to those expected for a pressure of about 5 kbar. The shortest Cu-Cu distances at ambient conditions are comparable to those found in (BEDT-TTF)₃CuCl₄·H₂O (8.576 Å) [10] but longer than those in (BEDT-TTF)₂CuCl₂ (6.676 Å) [11] or (BEDT-TTF)CuCl₂ (5.781 Å) [12]. The angle between the plane of the anion and *bc* plane is 13.18(3)° at ambient conditions, increasing to 13.46(4)° at 10 K, and to 14.1° at 10 kbar.

Fig. 5. — Anionic cavity with short Cu...C contacts (---) and hydrogen type contacts (<- - ->).

3.4.2. Variation of the Anion-Cation Contacts. — The anion is symmetrically surrounded by cations because of the presence of a centre of inversion at the copper. The CuBr_4^{2-} is adjacent to the BEDT-TTF^+ (A) and the neutral BEDT-TTF (B) sits in the cavities (Fig. 5). This particular position leads to short distances between the copper and one of the carbon atom of the extremities of the (BEDT-TTF). At one of its extremities, molecule A develops shorter contacts (3.469 Å) than at the other extremity (4.846 Å) or than B (4.674 Å). These distances decrease with increasing pressure or lowering temperature. However, their environments remain the same around the copper atoms. The distances between copper or bromine and sulphur are also quite short under ambient conditions and even shorter for A (Cu-S: 4.539 Å, Br-S: 3.649 Å) than for B (5.513 Å and 3.735 Å respectively). These distances decrease continuously with pressure but less for A (4.49 Å and 3.58 Å at 10 kbar) than for B (5.40 Å and 3.58 Å). At low temperature, they do not decrease for A (4.53 Å and 3.67 Å at 10 K) and only weakly for B (5.45 Å and 3.67 Å). So, the anion environments of A and B appear less different under pressure and at low temperature. There are short Br-H distances to both A and B (2.84 Å and 2.80 Å) that form angles of 157° and 169° at ambient conditions. If the distances decrease under constraints, the angles are nearly equal at 10 K and 10 kbar.

4. Variation of the Intramolecular Conformations

4.1. BEDT-TTF. — Disorder of the ethylene extremities of the kind frequently observed in BEDT-TTF molecules is not present in $(\text{BEDT-TTF})_3\text{CuBr}_4$, as may be seen from the normal C-C bond lengths of 1.53 Å and angles of 113°. The two ethylene bonds of molecule A are staggered and those of molecule B are eclipsed when viewed down the central C=C bond. The central parts of the BEDT-TTF are nearly planar under all conditions. The averaged central bond lengths of the two crystallographically unequivalent BEDT-TTF are different at room temperature but become closer at low temperature (see Tab. IV).

We have recently carried out a thorough statistical analysis of a large number of well characterised BEDT-TTF charge transfer salts and derived the charge carried by each BEDT-TTF from its intramolecular bond lengths [13]. This method has been tested successfully for

Table IV. — *Estimated charge of the ET molecules at different temperatures.*

	<i>T</i> (K)	entity	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>d</i> (Å)	δ (Å)	charge
ET ₃ CuCl ₂ Br ₂	298	A	1.376	1.725	1.743	1.357	0.735	0.86
	298	B	1.349	1.753	1.755	1.345	0.814	0.27
ET ₃ CuBr ₄	298	A	1.367	1.728	1.740	1.367	0.734	0.87
	298	B	1.345	1.757	1.762	1.332	0.842	0.06
	10	A	1.360	1.748	1.748	1.360	0.776	0.56
	10	B	1.377	1.739	1.755	1.353	0.764	0.65

Fig. 6. — Labelling of the averaged intramolecular bond lengths in BEDT-TTF used in the charge estimation.

structures with *R* factors less than 8% and on bond lengths with standard deviations no greater than 0.01 Å. It is based on the linear variation of the charge with the distance δ defined as

$$\delta = (b + c) - (a + d)$$

where *b*, *c* are the S-C and *a*, *d* the C=C averaged bond lengths of the central TTF (Fig. 6). This method has proved accurate to about 10% on the value of the charge. We apply this analysis to the structural information on (BEDT-TTF)₃CuBr₄ under ambient conditions and at 10 K. The results are collected in Table IV. We can note that the total charges are in good agreement with the theoretical ones. We find that the BEDT-TTF (A) on general position each carries +1 charge whilst the one (B) on the centre of inversion is neutral at room temperature. Thus the sequence in the stacks is A⁺A⁺B⁰ in agreement with the optical properties [2]. In contrast, it is equally clear that at 10 K, both BEDT-TTF (A and B) have almost the same charge. The cationic stacks are then built on the sequence A^{2/3+}A^{2/3+}B^{2/3+}.

It is important to emphasise that such charge delocalisation is quite unique among BEDT-TTF compounds. All the materials studied at low temperature and high pressure ((BEDT-TTF)₃Cl₂.2H₂O [7], α' -(BEDT-TTF)₂Ag(CN)₂ [8], α' -(BEDT-TTF)₂AuBr₂ [5] and (BEDT-TTF)₄Cl₂.6H₂O [14]) show the opposite tendency, the molecules becoming more different at low temperature in agreement with the observed electrical conductivities. Such a delocalisation of charge is consistent with the fall in activation energy at the transition.

The structure determined at 130 K is not accurate enough to apply the statistical approach but we can note that the averaged bond lengths of the two cations are very different, as at room temperature. It is also worth noting that the same method predicts equivalent charges on each of the three independent cations in (BEDT-TTF)₃CuCl₄.H₂O and very different ones for the two independent cations of the isostructural (BEDT-TTF)₃CuBr₂Cl₂ at room temperature and ambient pressure.

4.2. THE SHAPE OF THE ANION. — The anion CuBr₄²⁻ is found to be exactly square planar under ambient conditions. To our knowledge, no square planar CuBr₄²⁻ has been reported

Table V. — *Transfer integrals (meV) and difference in site energy Δ (meV) for $ET_3CuCl_2Br_2$ (1) and ET_3CuBr_4 (2).*

Transfer integrals	(1)	(2)				
Temperature	298 K	298 K	130 K	10 K	298 K	298 K
Pressure	1 bar	1 bar	1 bar	1 bar	4.5 kb	10 kb
Interaction						
A-A: a_1	54	54	50	44	45	29
A-B: a_2	0	0	0	25	0	0
A-B: d	50	49	58	50	57	63
A-A: c	76	66	74	73	71	80
A-B: b	140	134	151	162	145	152
A-A: e	71	68	69	73	71	85
Site Energy, Δ	400	400	400	0	-	-

previously for BEDT-TTF salts in contrast to the $CuCl_4^{2-}$ which adopts a square planar geometry in a number of cases. BEDT-TTF salts with other square planar anions have been reported, for example β -(BEDT-TTF) $_2$ AuCl $_4$ or β -(BEDT-TTF) $_2$ Au(CN) $_2$ Cl $_2$ [15].

The space group (P2 $_1$ /c) remains unchanged at low temperature, with the Cu still on a centre of inversion. The anion retains its square planar geometry contrary to what has been expected to explain the change in the g factors at the 60 K phase transition. We have also carried out a refinement in the Pc space group which allows the Cu to depart from the centre of inversion, but even in that case, the anion remains square planar.

The thermal vibration factors are very small whichever constraint is applied. At ambient the two Cu-Br bonds differ (2.407 Å and 2.421 Å). The bond lengths are equal at 130 K but slightly increase at 10 K where there are still different (2.413 Å and 2.437 Å).

5. Electronic Interactions

The transfer integrals between neighbouring molecules (see Tab. V) have been calculated from the Hückel method using a double- ζ basis set [16]. At ambient, the values within the chains are very small. This is common in the BEDT-TTF salts, see for example the (BEDT-TTF) $_3$ CuCl $_4$, H $_2$ O [9] or (BEDT-TTF) $_3$ Cl $_2$, 2H $_2$ O salts [17].

The zero value of the a_2 interaction comes from the difference between the bond lengths of the two cations. If we place a cation with the intramolecular conformation of A at the centre of gravity of B we calculate a transfer integral for a_2 of 30 meV. This is consistent with the difference between the charges of the two cations at ambient conditions.

On increasing the pressure, the intrachain interactions decrease as the interchain interactions increase. The change from 300 to 130 K is similar to that expected for the application of a modest pressure. At 10 K, the value of a_2 is no longer zero. Moreover, the values of the energy difference between the sites of cations A and B, which are very high at 298 K (400 meV) and 130 K (400 meV), are equal to zero at 10 K (Tab. V). The latter comes from the difference between the charges carried by the two cations. Hence the variation of a_2 and of the site energies agree with the disappearance of charge localisation below the transition.

Fig. 7. — Pressure dependence of the cell parameters of ET_3CuBr_4 .

Table VI. — Summary of crystal parameters determined for organic conductors: volumic variation, pressure of transition (P_t), pressure of loss of crystalline state (P_{limit}), bulk modulus at 1 bar and at the P_{limit} .

Salts	Ref.	$\Delta V/(V\Delta P)$ ($10^{-3} \text{ kbar}^{-1}$)	$B_{1\text{bar}}$ (kbar)	P_t (kbar)	P_{limit} (kbar)	B_{limit} (kbar)
α' - $\text{ET}_2\text{Ag}(\text{CN})_2$	[8]	8.5	87	8	13	188
α' - ET_2AuBr_2	[5]	8.3	91	7	11-14	180
κ - $\text{ET}_2\text{Cu}(\text{NCS})_2$	[8]	6.5	122	no	13	200
κ - $\text{ET}_2\text{Cu}(\text{N}(\text{CN})_2)\text{Cl}$	[21]	6.5	?	8	11	?
ET_3CuBr_4	-	5.9	127	5	14	210
$(\text{TMTSF})_2\text{PF}_6$	[19]	7.9	96	11	12	132
TTF-TCNQ	[20]	7.8	114	?	?	?
$(\text{TMTSF})_2\text{ClO}_4$	[19]	7.7	127	11	14	121

6. Cell Parameters

6.1. VARIATION WITH PRESSURE. — Figure 7 shows how the cell parameters decrease with pressure. The largest changes occur in the c parameter, while the a parameter scarcely changes. In all the studies of the crystallographic cell parameters of BEDT-TTF salts with pressure (see Tab. VI) or temperature [5, 7, 8, 14] we observe that the variation is strongly anisotropic. The largest variation is in the direction corresponding to the intrastack axis (c in the present case) then the direction corresponding to the interstack spaces (here close to b) and the direction corresponding to the alternating anion and cation sheets (here close to a) hardly varies.

Overall, there is little change in the cell volume over the pressure range studied which indicates that $(\text{BEDT-TTF})_3\text{CuBr}_4$ salt is not very compressible. Closer examination of the curves in Figure 7 reveals a slight break at around 5 kbar, which is the pressure at which the transition occurs between semiconducting and metallic states.

Fig. 8. — Isothermal compressibility tensor of ET_3CuBr_4 .

6.2. ISOTHERMAL COMPRESSIBILITY. — The amplitudes of the three principal directions of the compressibility tensor are k_1 , k_2 and k_3 . The amplitude of the first corresponds to the inter sheet space, the second to the space between stacks in the same layer and the last one to the intra stack space, as explained above. k_1 and k_3 lie within the ac plane as k_2 corresponds to b because of the monoclinic symmetry. Under ambient conditions, k_3 makes an angle of 18° with c . The directions of compressibility change slightly with pressure, the angle of k_3 and k_1 with c and a respectively increasing by only 6 from 1 bar to 13.5 kbar. For comparison the variation is about 14 in the α' salts $(\text{BEDT-TTF})_2\text{X}$ ($\text{X} = \text{Ag}(\text{CN})_2$ or AuBr_2) salt [5, 8] over similar pressure interval. The compressibility is strongly anisotropic ($k_1 : k_2 : k_3$) = (0.2 : 0.3 : 1) (Fig. 8), and the amplitude of k_3 that dominates the variation decreases strongly across the whole range, becoming of the same magnitude as k_2 at around 12 kbar. The anisotropy at 13.5 kbar is then (0.2:1.2:1).

At ambient conditions, the bulk modulus (k_v^{-1}), 127 kbar, reflects the poorly compressible character of the salt. Its limiting value, 210 kbar, is the highest observed among all the BEDT-TTF salts studied (see Tab. VI), though close to that found in the κ -(BEDT-TTF) $_2\text{Cu}(\text{NCS})_2$ salt [18]. Finally, Table VI shows that the bulk modulus of (BEDT-TTF) salts are higher than those of TMTSF salts and that α' salts seem to be more compressible than κ one.

6.3. LOSS OF CRYSTALLINITY. — At pressures higher than 14 kbar no reflections are detected. The intensity profile of the reflection 2, $-1, 7$ (Fig. 9) as a function of pressure shows how the peak disappears progressively. This effect cannot be reversed by lowering the pressure, even after six months. In fact, this phenomenon is common to all the salts studied at high pressure (Tab VI) [19, 20] and occurs at very similar pressure values due to the loss of mosaicity of the crystals. In many cases, it is preceded by a transition at lower pressure. Schultz *et al.* [21] reported that the phenomenon was reversible but this result has not been obtained in any other case.

From an experimental point of view, this seems to indicate that to carry out crystallographic studies of organic conductors at high pressure it is not necessary to reach pressures higher than 20 kbar. Hence, in the future, it will be possible to use bigger pressure cavities prohibiting very high pressure but allowing the use of larger crystals and higher diffracting volumes.

Fig. 9. — Intensity profile of a reflection as a function of pressure of ET_3CuBr_4 .

Fig. 10. — Temperature dependence of the cell parameters of ET_3CuBr_4 .

6.4. VARIATION WITH TEMPERATURE. — The a and b parameters scarcely change with temperature, while the c parameter decreases more. In general, the evolution of the cell with the temperature is very weak (Fig. 10). The 3% decrease in cell volume from 300 to 100 K is similar to that found in the $(\text{BEDT-TTF})_x\text{Cl}_2 \cdot y\text{H}_2\text{O}$ ($x = 3, y = 2$ and $x = 4, y = 6$) salts [7] and $\alpha'-(\text{BEDT-TTF})_2\text{X}$ [8]. As far as the absolute values of the cell constants are concerned, cooling to 10 K is equivalent to applying a pressure of around 5 kbar. A similar conclusion was reached for the α' salts. In fact, for this compound, the structural analysis also leads to the same conclusion.

6.5. ISOBARIC THERMAL EXPANSION. — The isobaric thermal expansion tensor of $(\text{BEDT-TTF})_3\text{CuBr}_4$ has been calculated only in the range 200 K – 100 K because of the large values of the standard deviations on the cell parameters at high temperature. The principal directions are close to those of the isothermal compressibility tensor. The angle between α_3 and the c axis increases from 8° at 200 K to 30° at 100 K, greater than that under pressure but comparable

with the α' salts. Overall the variation is similar to that observed as a function of pressure: α_3 and α_V decrease as α_2 increase and α_1 does not change. The anisotropy value is also comparable with that under pressure, (0.3 : 0.6 : 1) at 200 K and (0.1 : 1.1 : 1) at 100 K. The bulk modulus of this salt is higher (11200 K) than those of the α' salts (8100 K) and close to that of the (BEDT-TTF)₃Cl₂ · 2H₂O (12700 K) at 100 K.

7. Conclusion

(BEDT-TTF)₃CuBr₄ presents a new behaviour among the many charge transfer salts of BEDT-TTF [22], in that, on cooling, charge becomes more equally distributed between the organic cations. Pressure leads to closer contacts between (BEDT-TTF) of adjacent stacks. It is still not clear how the structural behaviour of this salt relates to its physical properties but the explanation previously proposed for the magnetic behaviour appears in contradiction with the structural results. The crystallographic results require the physical properties of this salt at low temperature to be re-examined.

We have been able to gain access to different points of the temperature-pressure phase diagram of (BEDT-TTF)₃CuBr₄; this study gives clear evidence that the crystal structures may be related to the physical properties only if they are both in the same conditions of temperature and pressure. The installation of a coupled system for X-ray diffraction at low temperature (10 K) under high pressure (0-30 kbar) is in progress in our laboratory with yet some good results and will constitute a powerful instrument for investigating many problems in organic materials.

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