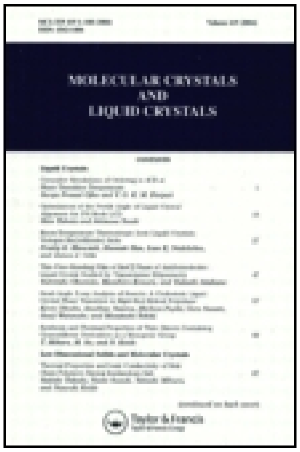

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The Effects of Crystal Packing on the Electrical Properties of the BEDT-TTF Charge Transfer Salts Containing Tetrahedral Anions (XO_4^-)

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A systematic comparison of the various crystal phases of the (BEDT-TTF):XO_4 [BEDT-TTF or "ET" is bis(ethylenedithio)tetrathiafulvalene, $C_{10}S_8H_8$; and XO_4^- is a tetrahedral inorganic anion] reveals that the electrical properties of these materials are directly related to their stoichiometries and crystal packing motifs. The formation of different crystalline phases is determined by the crystal packing requirements. Since the packing interactions between the anions and the ET molecules are determined by the (ethylene group)-$C_2H_4\cdots O$ type interactions, the conformational flexibility of the ethylene groups in the ET molecules is the probable cause for the variations in stoichiometry and crystal phases observed in these systems.

Keywords: organic conductors, electrical properties, crystal structure, BEDT-TTF

INTRODUCTION

Recently, many charge transfer complexes of the S-based organic donor molecule, BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene, $C_{10}S_8H_8$ or ET], of the form $(\text{BEDT-TTF})_nX_m$ [X is a monovalent

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inorganic anion] have been synthesized which possess unusual electrical properties. The first of these compounds, $(ET)_2(ClO_4)(TCE)_{0.5}$, where TCE is trichloroethane, exhibits two-dimensional (2D) metallic properties to a temperature as low as ~1.4 K.[1-3] The nonsolvated compound, $(ET)_2ReO_4$, remains metallic to ~81 K under ambient pressure at which temperature a metal-insulator (MI) transition occurs.[4] This MI transition can be suppressed under pressure ($P > 4.5$ kbar), and $(ET)_2ReO_4$ becomes superconducting at $T \sim 2$ K. Shortly after the discovery of superconductivity (SC) in $(ET)_2ReO_4$, the first sulfur-based *ambient pressure* organic superconductor, β-$(ET)_2I_3$ ($T_c \sim 1.6$ K),[5-8] was reported in 1984. Two isostructural trihalide derivatives of the triiodide salt, β-$(ET)_2IBr_2$ ($T_c \sim 2.5$ K)[9] and β-$(ET)_2AuI_2$ ($T_c \sim 5.0$ K)[10] were also found to be ambient pressure organic superconductors with the latter T_c being the highest reported to date. Several studies of the ET:trihalide (and pseudo-trihalide) salts have shown that the electrical properties of these ET charge-transfer compounds depend systematically on the packing motifs adopted by the ET molecules which, in turn, change with anion size.[11,12]

For tetrahedral inorganic anions (XO_4^-) such as ClO_4^-, BrO_4^- and ReO_4^-, the number of different phases of the ET:XO_4^- salts is numerous. Often, even with the same anion, the resulting charge-transfer salts obtained via electrocrystallization growth techniques [21] have several different stoichiometries and different crystal phases.[13,14,18] At least five different stoichiometries in this series of ET:XO_4^- compounds are known: (i) $(ET)_2(XO_4)$[4,15]; (ii) $(ET)_3(XO_4)_2$[16,17]; (iii) $(ET)_2(XO_4)(TCE)_{0.5}$[1-3]; (iv) $(ET)_2(XO_4)(THF)_{0.5}$[18]; and (v) $(ET)(XO_4)(THF)_{0.5}$.[19] In addition, three different crystalline phases of the $(ET)_3(ReO_4)_2$ salts are also known to exist.[20] The electrical properties and crystallographic data of these materials are summarized in Table I. It can be seen that the crystal structures of these materials, as implied by their stoichiometries and space group symmetries, are different, and their electrical properties range from semiconducting, to metallic (1D or 2D) and to superconducting. In the present study, the structural features of the ET:XO_4^- compounds are correlated with their electrical properties.

DISCUSSION

The basic assumptions in the present analysis are derived from the general observations of crystal close-packing, commensurate crystal structures and electron/charge delocalization in the ET materials dis-

TABLE I

Summary of Crystallographic and Conductivity Data for the ET:XO_4^- Salts

Compound	Space Group	Unit Cell Vol. (Å^3)	Z	T(MI)	Comment
$(ET)_2ReO_4$	$P\bar{1}$	1565	2	81 K	metallic (1D)[b]
$(ET)_2(ReO_4)(THF)_{0.5}$[a]	?	?		—	semiconductor
$(ET)_3(ReO_4)_2$					
α	$P2_1/n$	2418	2	88 K	Peierls transition
β	$P2_1/c$	2430	2	—	semiconductor
γ	$P\bar{1}$	1222	1	~10 K	metallic
$(ET)(ReO_4)(THF)_{0.5}$[a]	$P2/c$	1948	4	—	semiconductor
$(ET)_3(BrO_4)_2$	$P\bar{1}$	1213	1	50 K	metallic
$(ET)_2(BrO_4)(TCE)_{0.5}$[a]	$P\bar{1}$	1668	2	—	?
$(ET)_2(ClO_4)(TCE)_{0.5}$[a]	$P\bar{1}$	1684	2	20 K	metallic (2D)
$(ET)_3(ClO_4)_2$	$P\bar{1}$	1182	1	170 K	metallic (1D)
$(ET)_2(ClO_4)(C_4H_8O_2)$	$P2/c$	1814	2	—	semiconductor
$(ET)(IO_4)(THF)_{0.5}$[a]	$P2/c$	1950	4	—	semiconductor
$(ET)_3(IO_4)_2$	$P\bar{1}$	1231	1	—	?

[a] THF = tetrahydrofuran; TCE = trichloroethane

[b] $(ET)_2ReO_4$ is a pseudo two-dimensional metal near room temperature, and it becomes a superconductor ($T_c \sim 2$ K) only under pressure > 4 kbar.

cussed herein. In general, atoms and molecules in a crystal tend to adopt a close-packing geometry to optimize the intermolecular contacts. In most cases, molecules tend to form commensurate crystal structures. For the ET containing materials which consist of alternating layers of ET molecules and of monovalent anions, the cation and anion layers are commensurate (i.e., the cation and anion layers can be described by a single unit cell for a given material). An example of an incommensurate lattice can been seen in the tetrathiafulvalene:pentaiodide [$(TTF)_7I_5$] system, in which the organic molecules and pentaiodide anions form two different lattices.[22] It has been suggested that the geometries of the ET molecules change systematically with their respective formal charges.[14] However, in all known ET charge transfer salts, the crystallographically independent ET molecules in the unit cells are observed to have the same geometries, such that mixed-valent ET molecules are not probable (see Table II).[23] As a result, for a formal oxidation state of $(ET)_n^{+m}$, the $+m$ charge tends to delocalize over the n molecules. Hence, the ET molecules in these charge-transfer salts can be considered partially oxidized.

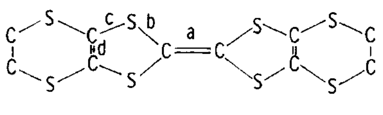
It appears that the seemingly diverse stoichiometries and different crystal packing geometries of these materials can be rationalized in

TABLE II

Intramolecular Bond Lengths (Å) of the ET Molecules in Some Selected ET:XO_4^- Charge Transfer Salts[a]

Compound	Formal Charge	a	b	c	d	T	Ref.
ET	0	1.32	1.76	1.75	1.33	298 K	25
$(ET)_2ReO_4$	+ 1/2	1.37	1.74	1.75	1.35	125 K	15
		1.37	1.74	1.76	1.36	"	
$(ET)_2BrO_4$	+ 1/2	1.37	1.74	1.75	1.36	125 K	15
		1.37	1.74	1.76	1.36	"	
$(ET)_2(BrO_4)(TCE)_{0.5}$	+ 1/2	1.38	1.74	1.76	1.36	125 K	17
		1.38	1.74	1.76	1.36	"	
$(ET)_3(BrO_4)_2$	+ 2/3	1.38	1.73	1.76	1.36	298 K	17
		1.37	1.73	1.74	1.36	"	
$(ET)_3(ClO_4)_2$	+ 2/3	1.37	1.73	1.74	1.34	298 K	16
$(ET)(ReO_4)(THF)_{0.5}$	+ 1	1.38	1.72	1.73	1.37	298 K	19

[a] The bond lengths are averaged over the chemically (but not necessarily crystallographically) equivalent bonds. When there is more than one crystallographically equivalent ET molecule in the unit cell, the averaged values for each ET molecule is given. The e.s.d.'s for the bond lengths are approximately 0.01 Å for the neutral ET structure. The corresponding e.s.d.'s for the other compounds are less than or the same as those in the neutral ET molecule. The bond lengths obtained from low temperature diffraction data are given whenever possible, although no significant differences have been observed for the same structures at two different temperatures.



BEDT-TTF, "ET"

Scheme I

terms of the formation of the charge-transfer complexes. Schematically, the formation of the ET charge-transfer salts by the electrocrystallization technique[6,21] can be considered as a sequence of events as in the following:

(*i*) $ET^\circ \rightarrow ET^+ + e^-$
(*ii*) $mET^+ + nET^\circ + mA^-/\text{solvent} \rightarrow (ET)_{n+m}A_m \cdot \text{solvent}$

Initially, the ET molecules in solution are electrochemically oxidized to form the + 1 cations. These cations can further combine with the neutral ET molecules and the counterions, A^-, (with or without solvent molecules) to form the charge-transfer salts. The stoichiometries of the final products, $(ET)_{n+m}A_m \cdot$ solvent, depend on the requirements of electrical neutrality of the solids and crystal close-packing. Thus, the presence of formally neutral ET and solvent molecules in the ET:XO_4^- salts can be considered to serve the purpose of space-filling. Hence, it is not surprising that the type and relative abundance of the different crystal phases has been observed to vary with the crystal growth conditions, such as that observed for the ET:ReO_4^- salts.[18] While the above scheme may not be the actual mechanism of the crystal growth, it is consistent with the observation that the charge-transfer salts of ET often co-crystallize in several different stoichiometries and different crystal structures all during the same electrocrystallization reaction.

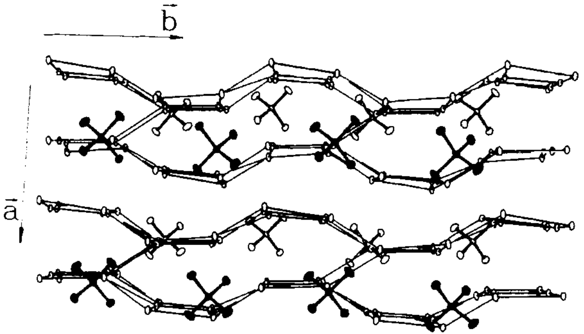
As shown in Table I, the different crystal phases of the ET:XO_4^- salts for any given anion have significantly different electrical properties. Therefore, it is concluded that the physical properties of these materials depends not only on the stoichiometries, but also on the crystal packing in the solids.

THE CRYSTAL STRUCTURES OF ET:X

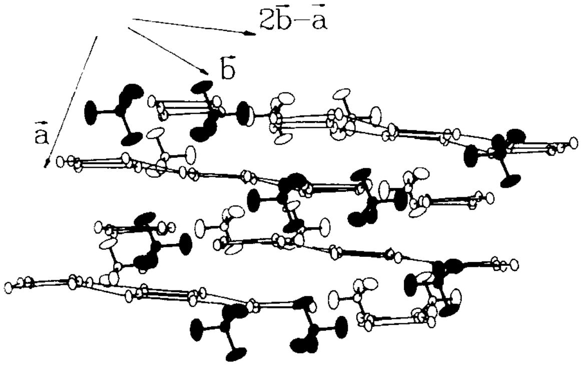
In general, the crystal structures of the ET charge transfer salts consist of layers of anions and cations. The typical crystal structures represented by the ET:BrO_4^- systems: (I) 2:1[15]; (II) 3:2[17]; and (III) 2:1:$(TCE)_{0.5}$[17] are illustrated in Figure 1. The crystal packing of these 3 materials are designated as types I, II and III, respectively, in this report. These compounds were chosen as representative of the ET:XO_4^- compounds because of the availability of the crystallographic data and known electrical properties. The crystallographic data of several selected compounds in this series are summarized in Table III.

The overall packing arrangement for these materials consists of alternating layers of anions and solvent molecules, and partially oxidized ET molecules (see Figure 1). Furthermore, the anions and solvent molecules can be considered to reside in the cavities defined mainly by the ethylene H atoms of the ET molecules (vide infra).

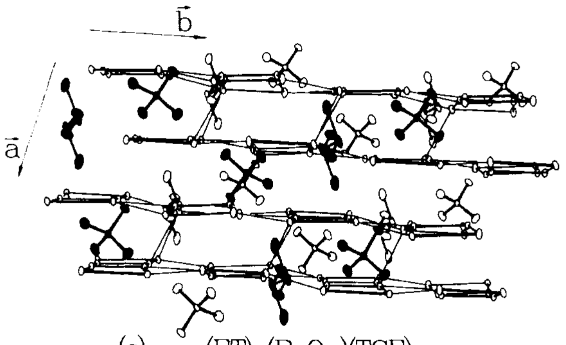
The unique crystal structure of $(ET)_2BrO_4$ is characterized by the loosely packed ET columns along the intrastack direction. Significant interstack S···S contact distances less than 3.60 Å (the sum of the sulfur atom van der Waals radii) also occur. Recent theoretical calculations have shown that such S···S close contacts do not necessarily contribute directly to the overall conduction band structure of the organic conductors.[2,24] In fact, such interstack S···S distances between the ET molecules have also been observed in the *neutral* ET solid.[25]



(a) $(ET)_2BrO_4$



(b) $(ET)_3(BrO_4)_2$



(c) $(ET)_2(BrO_4)(TCE)_{0.5}$

FIGURE 1 Illustrations of the two-dimensional ET network in (a) $(ET)_2(BrO_4)$; (b) $(ET)_3(BrO_4)_2$; and (c) $(ET)_2(BrO_4)(TCE)_{0.5}$. Only the S-atoms in the ET molecules were drawn and the short intermolecular S···S contact distances (<3.60 Å) were indicated by the thin lines. The anion (top layer with shaded ellipsoids) layers (including the solvent molecules in (c) were also included.

TABLE III

Unit Cell Parameters[a] of Some Selected ET:XO_4^- Salts

	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	V(Å^3)	Ref.
(A) $(ET)_2XO_4$								
ReO_4^-	7.798(5)	12.579(3)	17.102(6)	73.37(2)	80.35(2)	88.97(2)	1584(1)	4,15
BrO_4^-	7.795(2)	12.613(4)	17.148(5)	72.97(2)	80.44(2)	77.84(2)	1589(1)	15
(B) $(ET)_3(XO_4)_2$								
ReO_4^{-}[b]	8.498(3)	30.566(8)	9.413(3)	90.00	98.57(3)	90.00	2418(1)	20
	16.298(3)	12.013(3)	12.416(3)	90.00	91.24[d]	90.00	2430(1)	20
	11.744(2)	13.278(3)	16.859(4)	72.12(2)	77.78(2)	84.23(2)	2444(1)	20
BrO_4^-	7.670(1)	9.550(2)	16.686(2)	89.38(1)	87.02(1)	83.87(1)	1213(1)	17
ClO_4^{-}[c]	7.613(2)	9.498(2)	16.463(2)	89.16(1)	87.17(1)	84.09(2)	1182(1)	16
(C) $(ET)_2(XO_4)(TCE)_{0.5}$								
BrO_4^-	7.656(2)	12.957(4)	18.590(2)	109.6(2)	90.2(2)	105.1(2)	1668(1)	17
ClO_4^{-}[c]	7.740(5)	12.966(7)	18.519(13)	110.0(1)	90.4(1)	104.8(1)	1679(1)	1

[a] The unit cell parameters were obtained at 298 K, except for $(ET)_2(BrO_4)(TCE)_{0.5}$ which was obtained at 125 K. Except for $(ET)_3(ReO_4)_2$, the crystal structures in each class were observed to be isostructural.

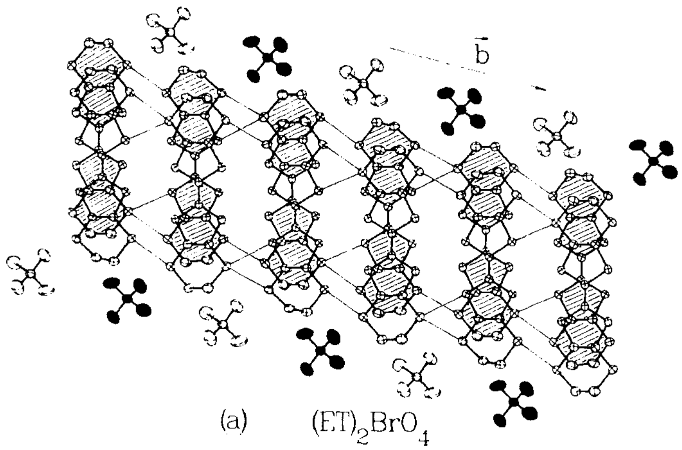
[b] None of the three phases of the $(ET)_3(ReO_4)_2$ salts are isostructural to the ClO_4^- and BrO_4^- analogs.

[c] Transformed unit cell parameters are used so that direct comparisons between the isostructural salts are possible.

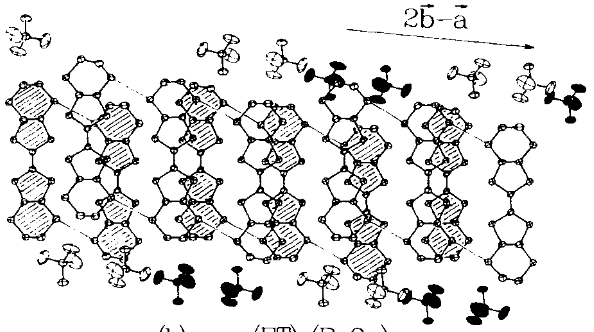
[d] No. e.s.d. given in reference 20.

Theoretical calculations using the extended Hückel method have shown that $(ET)_2BrO_4$ and $(ET)_2ReO_4$ have a 2D metallic band structure and that the most conducting axis in each of these materials is parallel to the column (intrastack) packing direction.[26]

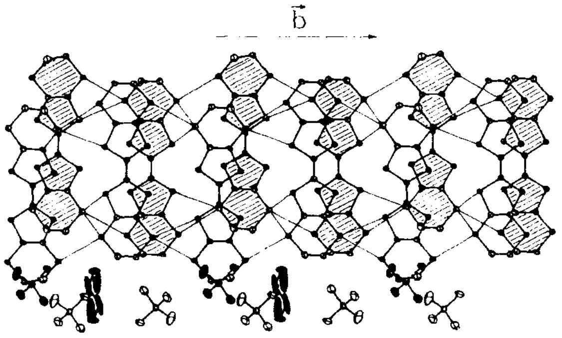
The projections of the ET network in II and III are similar (see Figure 1). In both cases, there are no distinct columns along the intrastack direction. Rather, there are two sets of possible intrastack interactions: along unit cell axes *a* + *b* and *a* for the type II structure, and along *b* and *a* + *b* for the type III structure. As judged from the packing geometries along the interstack directions, the intermolecular interactions along this direction can be characterized by $\pi(p_\pi - p_\pi)$ overlaps between adjacent ET molecules.[2] All other intermolecular interactions are of the $\sigma(p_\pi - p_\pi)$ type. The theoretical calculations on the band structure of $(ET)_2(ClO_4)(TCE)_{0.5}$, which is isostructural to the BrO_4^- analog, have shown that the two intrastack directions are not equivalent in terms of intermolecular overlap. Furthermore, these molecular overlaps are directly related to the band structure of the conducting materials. As shown in Figure 2, the interstack packing of the ET molecules in II and III are dif-



(a) $(ET)_2BrO_4$



(b) $(ET)_3(BrO_4)_2$



(c) $(ET)_2(BrO_4)(TCE)_{0.5}$

FIGURE 2 Illustrations of the interstack packing of the ET molecules in (a) $(ET)_2BrO_4$; (b) $(ET)_3(BrO_4)_2$; and (c) $(ET)_2(BrO_4)(TCE)_{0.5}$. Two rows of ET molecules and anions are included here.

ferent. As a result of the changes in the anion layer, the interstack ET packing must change accordingly to accommodate the anions and the solvent molecules. While the three ET networks are different, the average interplanar distances (per ET pair) of 3.76 Å, 3.75 Å and 3.74 Å for the type I, II, and III structures, respectively, are approximately the same along the "column" directions. The ET "column" directions (i) along the *a* axis in $(ET)_2BrO_4$, (ii) along $a + b$ in $(ET)_3(BrO_4)_2$, and (iii) along $2a + b$ in $(ET)_2(BrO_4)(TCE)_{0.5}$ are illustrated in Figure 1.

H···X INTERACTIONS BETWEEN THE ANION-CATION LAYERS

Now we turn to the observed patterns of the ethylene group conformations in these solids and how they influence the crystal packing and electrical properties. The two ethylene groups on opposite ends of an ET molecule can have either cis- or trans-conformations. In $(ET)_2BrO_4$, both of the crystallographically independent ET molecules adopt the trans-conformation, and the salt is crystallographically ordered. In $(ET)_3(BrO_4)_2$, the two independent ET molecules adopt the cis- and the trans-conformations, respectively. Finally, in $(ET)_2(BrO_4)(TCE)_{0.5}$, each of the two ET molecules has one disordered ethylene group. Hence, the cis- and trans-conformations are considered equally probable in the last structure. These differences in the ethylene conformations are consequences of the short anion···H contacts observed in these materials.

For most ET salts in this series of compounds, the anions are located in the cavities defined mainly by the H-atoms of the ethylene groups. Short O···H distances significantly less than the sum of their van der Waals radii (~2.7 Å) are often encountered in these materials (see Table IV), and these short distances are indicative of strong crystal packing interactions between the counterions. Such short O···H contact distances have also been observed previously in the $(TMTSF)_2X$ salts.[27-29] These packing interactions in the latter compounds have been shown to be significant in terms of anion-ordering superlattice structural transitions which can change the electrical properties of these organic metals. On the other hand, the shortest O···S distances in the ET:BrO_4^- salts are about the same as their van der Waals radii sum (3.30 Å). Two of the stable configurations of the ET molecules about the tetrahedral anions are illustrated (see Figure 3). The anions in $(ET)_2BrO_4$ are equally spaced and are isolated from each

TABLE IV

Intermolecular O···H Distances (Å) in Several Selected ET:XO_4^- Compounds[a]

$(ET)_2BrO_4$ [b,c]		$(ET)_2ReO_4$ [b,c]		$(ET)_3(BrO_4)_2$ [d]	
O(1)···H(10B)	2.49	O(1)···H(10B)	2.42	O(1)···H(10A)	2.58
O(2)···H(8B)	(2.74)[e]	O(1)···H(8B)	2.70	O(2)···H(7B)	2.56
O(2)···H(8A)	2.34	O(2)···H(8A)	2.26	O(2)···H(17B)	2.68
O(2)···H(19A)	2.44	O(2)···H(19A)	2.38	O(3)···H(7B)	2.49
O(2)···H(7B)	2.51	O(2)···H(7B)	2.41	O(3)···H(10B)	2.70
O(3)···H(9B)	2.37	O(3)···H(9B)	2.34	O(4)···H(9B)	2.39
O(3)···H(18B)	2.39	O(3)···H(18B)	2.31	O(4)···H(18B)	2.60
O(3)···H(17A)	2.68	O(3)···H(17A)	2.65		
O(4)···H(20A)	2.49	O(4)···H(20A)	2.43		

[a] All O···H distances less than or equal to 2.70 Å (the sum of the O and H van der Waals radii) were included. The H atomic positions used in the estimates of the O···H distances were calculated using the observed positions of the nonhydrogen atoms in the ET molecules and assuming sp^3-hybridized ethylene C atoms and a C—H bond length of 1.09 Å.

[b] The atom numbering scheme for the isostructural $(ET)_2BrO_4$ and $(ET)_2ReO_4$ are the same.

[c] The crystal structures obtained at 125 K were used.

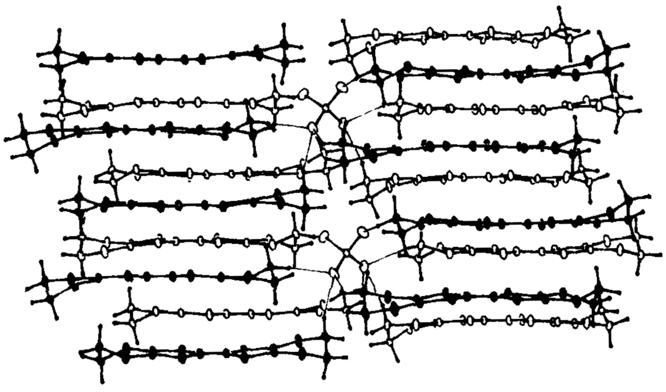
[d] The crystal structure was obtained at 298 K.

[e] The O(1)···H(8B) distance in $(ET)_2BrO_4$ is included for comparison purposes.

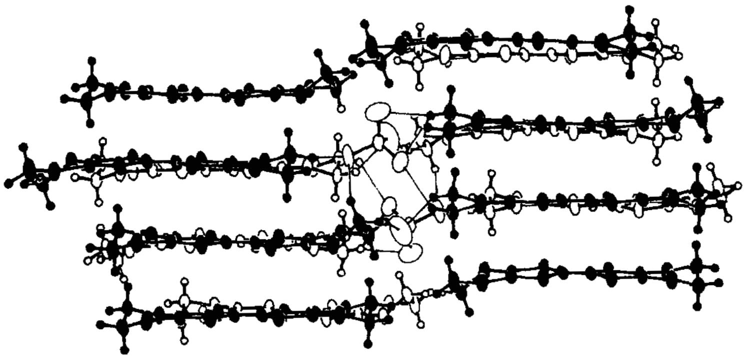
other since their respective close neighbors are the H-atoms. There are eight such short O···H contact distances for each anion. For $(ET)_3(BrO_4)_2$, the pairs of anions related by an inversion center are encapsulated totally by the H-atoms and the number of short O···H contacts for each anion is about the same as that for the type I compounds (see Table IV). The anions in the type II compounds are not equally spaced as are those in the type I compounds. Along both the interstack and the intrastack directions, the arrangement of the anions is in the form ···AA′XAA′··· (A and A′ are related by a center of inversion and X is a vacant site).

For $(ET)_2(BrO_4)(TCE)_{0.5}$, the crystal packing between the anion and cation layers is probably not very efficient because of the presence of disordered ethylene groups and solvent molecules, TCE. Analysis of the anion-cation interactions in terms of O···H contact distances is not possible because of the conformationally disordered ethylene group C-atoms, although significant packing interactions are expected between the counterions and between the ET and TCE solvent molecules.

Because of these O···H contacts and possible packing interactions between the ET and TCE molecules in $(ET)_2(BrO_4)(TCE)_{0.5}$, the structural differences in the types I and III structures can be ration-



(a) $(ET)_2BrO_4$



(b) $(ET)_3(BrO_4)_2$

FIGURE 3 Illustrations of the anion···H (ethylene) packing interactions in (a) $(ET)_2BrO_4$ (top) and (b) $(ET)_3(BrO_4)_2$ (bottom). The short O···H distances (<2.70Å) are indicated by the thin lines. The ET molecules in the front column are represented by the solid ellipsoids.

alized to occur as a result of solvent inclusion. For the type II and III structures, rearrangement occurs only for the interstack packing in the ET molecule 2D-network when the anion layers are changed. Finally, as the number of ET molecules in the unit cells and the formal charges of the ET molecules are different, the resulting band structures for these materials are expected to change accordingly.

EFFECTS OF ANION SIZES ON THE CRYSTAL STRUCTURES

The sizes of the tetrahedral anions XO_4^-, as estimated from the X—O distances (Re—O = 1.73 Å,[15] Br—O = 1.61 Å[15] and Cl—O = 1.45 Å[31]), decrease in the order: $ReO_4^- > BrO_4^- > ClO_4^-$. It appears that the ET-rich (or anion-deficient)[30] $(ET)_2XO_4$ salts favor the presence of larger anions such as ReO_4^- and BrO_4^-, whereas $(ET)_2ClO_4$ is not known. On the other hand, the ET-deficient $(ET)_2(XO_4)(TCE)_{0.5}$ salts favor smaller anions, and $(ET)_2(ReO_4)(TCE)_{0.5}$ is not known. The intermediate $(ET)_3(XO_4)_2$ stoichiometry appears to be suitable for all three anions. However, none of the three different crystal phases of $(ET)_3(ReO_4)_2$ are isostructural to the BrO_4^- and ClO_4^- salts. A meaningful comparison is not possible because of the lack of available structural data for the $(ET)_3(ReO_4)_2$ phases. Nevertheless, the size of the ClO_4^- anion can possibly be considered as the lower limit for a stable type I $[(ET)_2XO_4]$ structure, and that of the ReO_4^- anions as the upper limit for a stable type III $[(ET)_2(XO_4)(TCE)_{0.5}]$ structure.

CONCLUSION

In summary, the comparsion of the different ET:BrO_4^- materials reveals that the formation of different ET:XO_4^- phases is most likely determined by the crystal packing requirements. Furthermore, the packing interactions between the counterions are determined mainly by the O···H (ethylene groups) interactions. More importantly, because of the conformational flexibility of the ethylene groups in the ET molecules, several different stable crystal phases can exist simultaneously. The existence of different crystal phases and stoichiometries can be rationalized if the presence of "neutral" ET molecules and solvent molecules in the solid serves to satisfy the requirements of space-filling. Therefore, the abundance of each different crystal phase is expected to change with the crystal growth conditions such as the electrical current density at the electrodes, the type of solvent molecules and temperature.

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