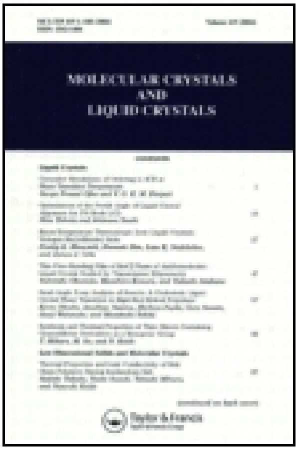

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The Many Faces of ET

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THE MANY FACES OF ET

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Abstract A major feature of the ET† molecule is its ability to form many different phases and structures with the same or different anions. Whilst this considerably complicates the growth and characterisation of these materials this does allow a systematic study of compounds differing only in charge state or crystal structure, but otherwise containing the same donor and acceptor species. We show that ET forms at least four different phases with the ReO_4^- anion, allowing such a systematic study. We show that one of these, γ-$ET_3(ReO_4)_2$, is the only currently known example of an ET charge transfer salt in which the anions are not ordered at room temperature. We find the anions become ordered at a lower temperature. We show that anions smaller than some certain value stabilise a single phase containing 3 ET molecules for every two anions and that larger anions form different sets of crystal structures.

1-INTRODUCTION

Almost two years ago superconductivity was found in $(BEDT\text{-}TTF)_2ReO_4$† for pressures above 4.5 kbar and temperatures below ≃2 K[1]. With the recent discovery of superconductivity by Yagubskii *et al* [2] in a second member of this family, $(BEDT\text{-}TTF)_2I_3$, at ambient pressure, ET has finally been brought down to earth.

Saito *et al* [3] first synthesized a charge transfer salt based on the ET molecule. We have subsequently synthesized many compounds based on ET containing a wide variety of anions ranging from small symmetric anions like Br^- to large asymmetric tetrahedral anions such as FSO_3^-. We have also attempted to grow by the same standard electrochemical procedures systems containing molecules which are slight modifications of ET, including BEDSe-TSeF[4], (ES), the selenium analogue of ET, and BVDT-TTF, (VT), in which the extreme C-C bonds at either end of the ET

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† we shall use the designation "ET" for BEDT-TTF

molecule are left unsaturated. The probable rationale for making these modifications was in the first case, the possibility of larger transfer integrals and in the second, the likelihood of improving the planarity of the ET molecule which might be expected to increase intrachain S-S interactions. These latter systems have so far proved to be rather disappointing. The BEDSe-TSeF salts we have been able to prepare all have 1:1 stoichiometries and are as a consequence insulating: we have only been able to grow reasonable crystals of one VT compound, $VT_3(FSO_3)_2$, which has properties very similar to its isostructural ET analogue.

In this paper we are going to describe a remarkable series of ET compounds which display quite different transport properties yet are all perrhenate salts.

2-LA GRANDE HYSTERIE

In contrast to the small number of BEDSe-TSeF and VT salts that we have been able to grow we have prepared large numbers of ET compounds including those shown in Table 1. It is interesting to note that all the anions in Table 1 form isostructural compounds with TMTCF[†] of the form $(TMTCF)_2X^5$, yet with ET the same anions

Table 1-Crystallographic Parameters for various BEDT-TTF$_x$X$_y$ Salts at 300 K

Anion	x:y	Space Group	Z	a	b	c	α	β	γ	Volume
ReO_4[a]	2:1	$P\bar{1}$	2	12.596(3)	17.117(4)	7.802(1)	99.55(2)	90.85(2)	73.46(2)	1589.3
α[a]	3:2	$P2_1/n$	2	8.498(3)	30.566(8)	9.413(3)		98.57(3)		2417.9
β[a]	3:2	$P2_1/c$	2	16.298(3)	12.013(3)	12.416(3)		91.24		2430.2
γ[ab]	3:2	$C\bar{1}$	2	11.744(2)	13.278(3)	16.859(4)	72.12(2)	77.78(2)	84.23(2)	2443.6
FSO_3[a]	3:2	$P\bar{1}$	1	9.421(8)	16.578(7)	7.605(6)	95.04(5)	96.89(9)	87.74(6)	1174.1
Br	3:2	$P\bar{1}$	1	9.606(2)	16.194(3)	7.743(1)	95.00(1)	99.05(2)	84.92(2)	1181.5
BF_4	3:2	$P\bar{1}$	1	9.496(3)	16.398(5)	7.654(5)	92.42(4)	96.09(4)	88.99(3)	1183.9
ClO_4[a]	3:2	$P\bar{1}$	1	9.513(1)	16.488(2)	7.620(1)	92.90(1)	95.98(1)	89.13(1)	1187.2
IO_4	3:2	$P\bar{1}$	1	9.303(1)	16.231(2)	8.418(2)	91.77(1)	97.33(2)	101.93(1)	1231.4
PF_6[a]	1:1	$C2_1/c$	4	33.827(17)	6.714(2)	8.293(5)		102.52(5)		1838.6

[a] *We have made complete structure determinations at room temperature for these compounds and at lower temperatures in several cases.*

[b] *The lattice parameters given for this phase correspond to a non-primitive cell in order that these values can be compared directly with those at low temperature described in a following section. The volume of the primitive room temperature cell, which has $P\bar{1}$ symmetry, is two times smaller. Note that below 200 K the ReO_4^- anions order resulting in a doubling in volume of the primitive unit cell.*

[c] *Z is the number of (BEDT-TTF$_x$X$_y$) units in the unit cell.*

[†] where C=Se (TMTSeF) or S (TMTTF).

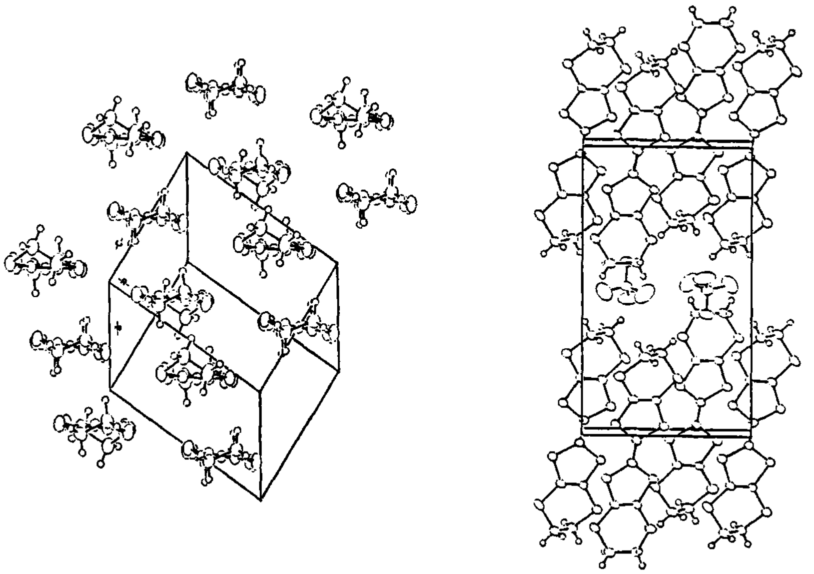

Figure 1: Views of the structure of ET$_3$(ClO$_4$)$_2$ at 300 K[6] along the long axis of the molecule and perpendicular to the plane of the molecule.

form salts of various stoichiometries and a bewildering number of different structures. However for many of the smaller anions a single phase with stoichiometry of 3:2[‡], (i.e. ET$_3$X$_2$) is formed. The structure for a typical example, the ClO$_4$ salt which we have studied in some detail[6], is shown in figure 1.

In figure 2 we plot the unit cell volumes, V, of the δ-ET$_3$X$_2$ salts versus those of the corresponding TMTTF$_2$X salts. We also include for comparison the same plot for the TMTSeF$_2$X compounds[7]. In the latter case V of TMTSeF$_2$X is linearly proportional to that of the corresponding TMTTF salt, indicating V simply increases in proportion to the size of the anion. Thus, we shall use V of TMTTF as a measure of the size of the anions[†]. If this were also true for the δ-ET$_3$X$_2$ salts we would

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[‡] we shall label this phase as the δ phase.

[†] Note that Williams *et al* (Phys. Rev. B28, 2873 (1983)) have recently argued on the basis of comparisons of lattice parameters and interchain contacts versus *calculated* anion volumes for TMTSeF$_2$X that the ClO$_4$ salt, which is superconducting at ambient pressure, possesses some sort of special but undefined selenium network. We point out that these conclusions are quite wrong and are based on an incorrect assignment of anion volumes. When these distances and lattice parameters are plotted versus unit cell volume we find a monotonic variation of all parameters with V. Certain pancake shaped anions, for example H$_2$F$_3$, do show anomalously large values of certain parameters (e.g. b and the associated interchain Se-Se contact) because the anion is much longer in these directions compared to its anion volume than other more symmetric anions. Also note that no detailed crystal structure determination is required to consider variations of interchain Se-Se contacts since these are simply proportional, as expected from the crystal structure, to the b lattice parameter.

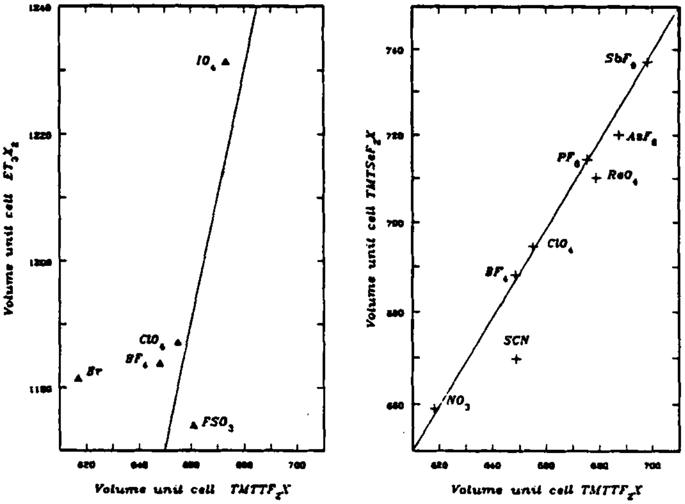

Figure 2: Plot of the unit cell volume of (a) δ-ET_3X_2 and (b) $TMTSeF_2X$[7] versus that of the corresponding $TMTTF_2X$ compound. We expect linear variations with slopes of respectively 2 and 1. These are the solid lines shown in the figure. Note that we have estimated the unit cell volume of $(TMTTF)_2IO_4$ since this material has not been prepared.

expect a linear variation with slope two since the unit cell of the ET salt contains twice as many anions as the TMTTF salt. As can be seen from figure 2 we find a very different behaviour in which *V* of δ-ET_3X_2 is approximately constant at small anion volume (small *V* for $TMTTF_2X$) for anions ranging in size from Br^- to the much larger FSO_3^- anion. These data thus suggest that the size of the cage of ET molecules in which the anions sit is formed independently of the anion and is determined by some preferred arrangement of organic molecules. One might expect that when the anion size is increased to fully accommodate the volume of the cage, *V* would increase. Figure 2 suggests that this point is reached for an anion intermediate in size between FSO_3^- and IO_4^- since *V* is considerably increased for the latter salt.

For anions a little larger than those shown in figure 2(a) we no longer find the δ phase but a number of other quite distinct phases of which perhaps the most remarkable is that exhibited by ET-PF_6[8]. The structure of this material contains stacks of criss-crossed ET molecules as shown in figure 3. In addition to this 1:1 ET-PF_6 salt two phases of the form ET_2PF_6 have been found by Kobayashi *et al*[9]. For the ReO_4^- anion we have so far identified four distinct crystalline phases as described further below. For still larger anions a quite different set of structures are found (TaF_6[10]; SbF_6[11], AsF_6[11]). There is thus a markedly different behaviour between smaller and larger anions: in the former case a single structure of 3:2 stoichiometry is found whereas in the latter a multitude of different structures and stoichiometries are formed.

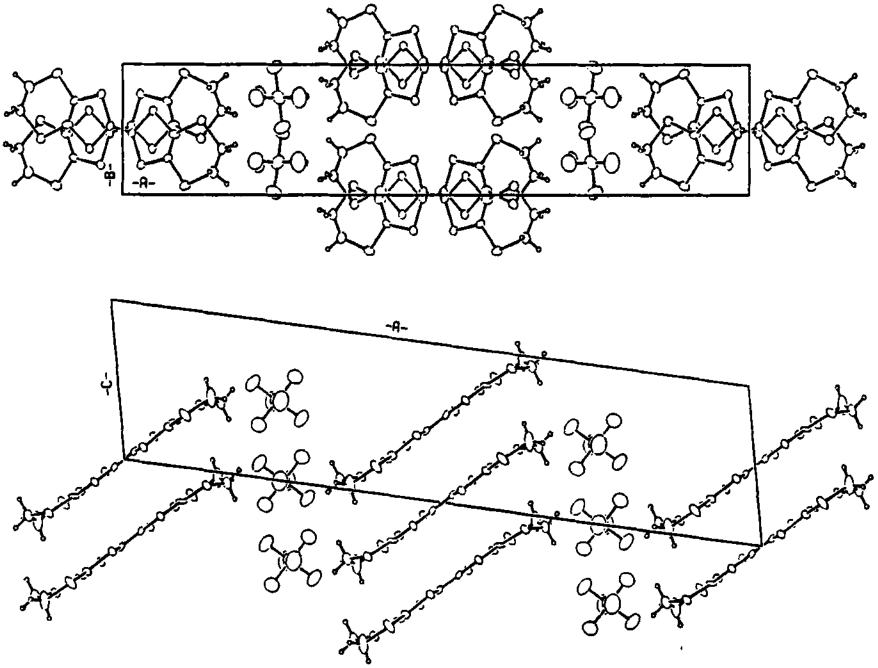

Figure 3: The structure of ET-PF_6 at 300 K[8].

3-THE STRUCTURE OF $(ET)_2ReO_4$

A view of the structure of (BEDT-TTF)$_2$ReO$_4$ along the stacking axis is shown in figure 4[1]. It is immediately obvious that the structure strongly resembles that of the (TMTCF)$_2$X salts. There are planes of molecular stacks separated by planes of ReO_4^- anions. Moreover the ET molecules are slipped with respect to each other along any given stack in a similar way to that of the TMTCF molecular stacks as demonstrated in figure 5 where the structure of (BEDT-TTF)$_2$ReO$_4$ is compared to that of (TMTTF)$_2$ReO$_4$[12]. There are however some important differences between the structures of these families. In (BEDT-TTF)$_2$ReO$_4$ and all the ET salts we have prepared with one exception, namely γ-ET$_3$(ReO$_4$)$_2$, the anions are ordered. With respect to the primitive unit cell conventionally chosen for the (TMTCF)$_2$X salts (see figure 4) the anion ordering in (BEDT-TTF)$_2$ReO$_4$ can be described by a wave vector, $\underline{Q} = (0,1/2,1/2)$. This is the same anion arrangement which when it takes place below 160 K in (TMTTF)$_2$SCN drives the material insulating[13] and yet the ET salt is metallic!

Figure 5 also demonstrates one other obvious way in which the ET and TMTCF salts differ: the TMTTF molecule is considerably flatter than the ET molecule and this is generally true as we shall discuss further below. The aplanarity of the ET

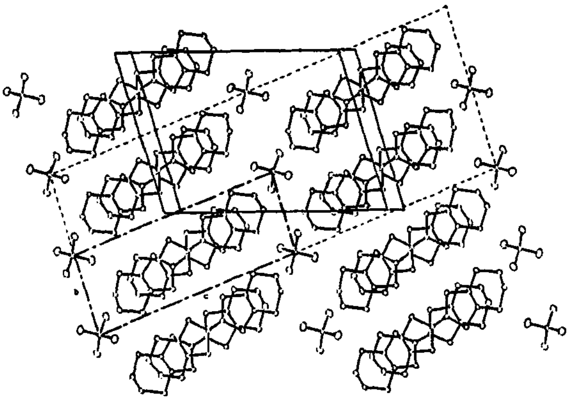

Figure 4: View along the a axis of (BEDT-TTF)$_2$ReO$_4$[1]. The primitive cell is shown in solid lines. Also shown in dashed lines is the primitive unit cell corresponding to that of the (TMTCF)$_2$X (C=Se,S) salts. The unit cell of (BEDT-TTF)$_2$ReO$_4$ is a (0,2b,2c) supercell of the smaller cell.

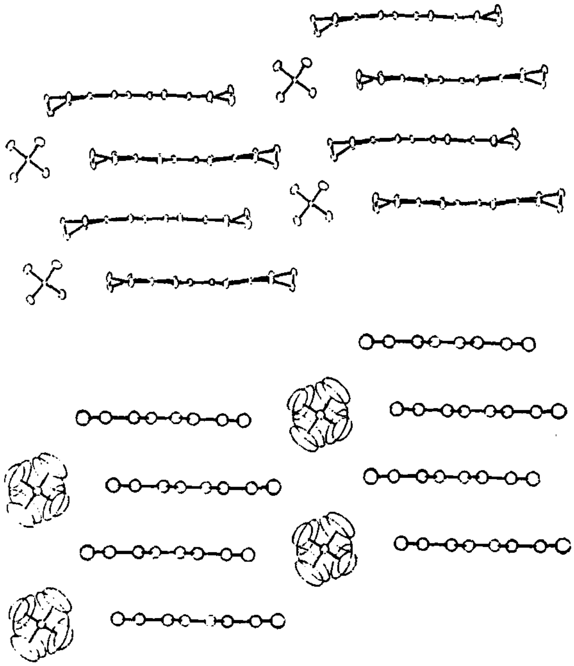

Figure 5: View perpendicular to the molecular stacking axis in (a) (BEDT-TTF)$_2$ReO$_4$ and (b) (TMTTF)$_2$ReO$_4$

molecule is mostly associated with the outer rings. In figure 6 we compare the bonding of the sulphur networks in (BEDT-TTF)$_2$ReO$_4$ and (TMTTF)$_2$ReO$_4$. We

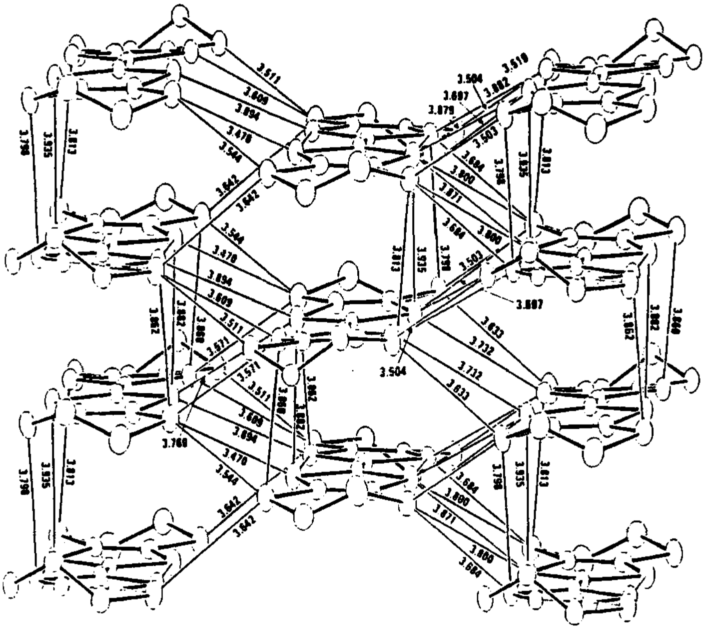

Figure 6(a): Sulphur sulphur contacts shorter than 4.0Å in $(BEDT\text{-}TTF)_2ReO_4$

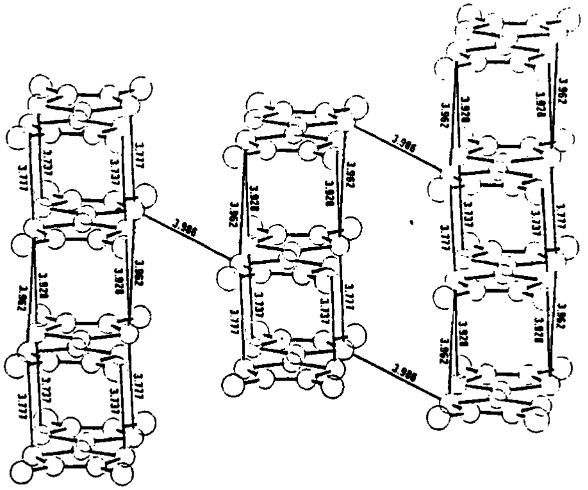

Figure 6(b): Sulphur sulphur contacts shorter than 4.0Å in $(TMTTF)_2ReO_4$

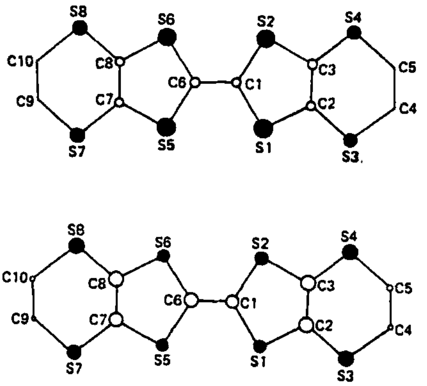

Figure 7: CNDO/2 calculation of the homo spin density and charge density for the centrosymmetric $ET^{0.5}$ molecule in $(BEDT\text{-}TTF)_2ReO_4$

only show bonds less than 4.0Å in length. Often the bonding in organic compounds is compared with bond lengths derived from van der Waals radii. For example Pauling[14] suggests a radius for S of 1.85Å implying a S-S bond distance of about 3.7Å. Figure 6 shows there are no intrastack S-S contacts shorter than the Pauling bond length in $(TMTTF)_2ReO_4$ (the minimum distance is ≃3.74 Å long) yet the calculated band width along the stack for this material is of the order of 0.8 eV![15] One must be very careful in blindly writing off bonds longer than the van der Waals distance[†]. In considering the magnitude of the overlap integral associated with a particular S-S bond one must take into account two other important parameters, the spin density on the S atom and the angle the S-S bond makes with the plane of the molecule. We have calculated the spin density for the BEDT-TTF and TMTTF molecules using the CNDO/2[17] programs[‡]. The results are shown schematically in figure 7 for the $ET^{0.5}$ molecule (atomic positional parameters were taken from ref. 3). Note that the spin density (calculated from the sum of the squared coefficients of the homo wave function) is almost twice as large for the S atoms on the inner rings as it is for those on the outer rings of the molecule. This means that bonds between S atoms on the outer rings of two different $ET^{0.5}$ molecules will be approximately twice as weak as the bonds between S atoms on the inner parts of the molecules. Figure 7 also shows the CNDO/2 charge density calculated for the $ET^{0.5}$ molecule: in contrast with the spin density distribution the charge density is greater for the S atoms on the outer rings of the molecule. These results thus sug-

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[†] Note that elsewhere in these proceedings Williams *et al*[16] state that the ET_2X salts, including the ReO_4 salt, possess a very unusual S-S bonding network with no significant intrastack S-S interactions. We suggest these statements are incorrect since they are based on ignoring S-S bonds longer than some arbitrary value set at 3.6Å. Moreover note that the intrastack S-S bond lengths in ET_2ReO_4 are comparable with those in $TMTTF_2ReO_4$ (compare Figures 6(a) and 6(b)).

[‡] I thank Prof. R.M. Metzger for kindly providing me with copies of these programs.

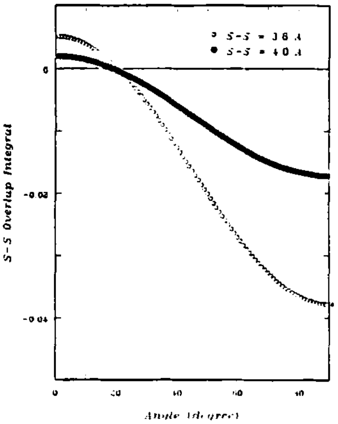

Figure 8: Sulphur-sulphur overlap integral (see text) as a function of angle, ϕ, between the S-S bond and the plane of the molecule containing one of the S atoms for S-S separations of 3.6 and 4.0Å.

gest the inner rings of adjacent ET molecules are more strongly bonded and the outer rings more strongly repelled.

The homo orbital at the sulphur atom has strong p_z character (as we find for example by considering the CNDO/2 homo eigenfunction - note this function is also symmetric), which means that the overlap integral of wavefunctions on neighbouring S atoms is very sensitive to the relative position of the planes of the neighbouring ET molecules. In particular for the same S-S bond length it is obvious that the overlap integral will be much larger when the S atoms are in a σ configuration than when they are oriented in a π fashion. To simple-mindedly demonstrate this we have plotted in figure 8 the overlap integral, t, for two sulphur atoms separated by respectively 3.6 and 4.0 Å, as a function of the angle, ϕ, between the S-S bond and the plane of the molecule in which one of the S atoms reside. Note we have chosen ϕ such that $\phi=0$ (90°) when the S atoms are in the $\pi(\sigma)$ configuration. We have made use of analytical expressions derived by Mulliken *et al*[18] for the overlap integrals between Slater $3p\pi$ and $3p\sigma$ atomic orbitals. An important consequence of the different signs of t for the $p\pi$-$p\pi$ and $p\sigma$-$p\sigma$ interactions is that the S-S overlap passes through zero at some value of ϕ (see figure 8). Although the Slater orbitals fall off exponentially with distance from the atom centre, for the range of S-S contact-distances of interest in these systems the interaction actually varies quite slowly. We mentioned earlier that there is a larger spin density on the inner ring S atoms: figure 8 shows that in order that the overlap integral between two inner S atoms has the same value as t between two outer S atoms separated by for example 3.6Å, the inner S atoms will be much separated by about 4.0Å, a considerably larger distance. Care must be taken in over-interpreting bonding networks derived by including only S-S bonds smaller than some arbitrary value[16].

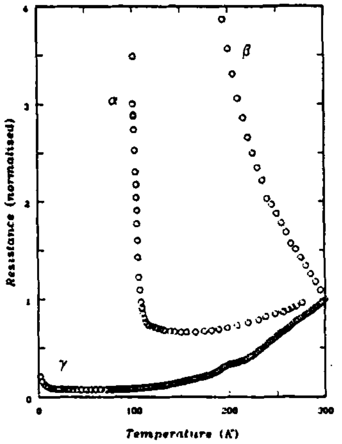

Figure 9: Resistivity curves for the α, β and γ $ET_3(ReO_4)_2$ phases.

4-α, β and γ $ET_3(ReO_4)_2$ [†]

In addition to ET_2ReO_4 we have found three distinct phases in which each anion is coupled with only 1.5 ET molecules (see Table 1 for labelling and crystallographic parameters). These phases display quite different transport properties as is demonstrated in Figure 9 where the electrical resistance versus temperature curves of these three phases are compared. The β phase is an insulator at room temperature whilst both the α and γ phases are metals at these temperatures. The α phase shows a sharp metal-insulator transition near 100 K: the transition temperature decreases as pressure is increased[8]. The γ phase is metallic to very low temperatures but exhibits a weak preparation-dependent upturn in resistance below ≃10 K.

The very different character of these compounds can be understood by considering their quite different crystal structures. A detailed study of the structure of β-$ET_3(ReO_4)_2$ shows this system has a highly one-dimensional structure with weak interstack coupling. Note that for a one dimensional stack of ET molecules with charge state +0.67 (ignoring correlation effects) the conduction band is 1/3 full. The electronic system is thus unstable to potentials with a component of wavevector along the stack of $2\,\underline{k}_F = 4\,\underline{k}_F = 1/3\,\underline{a}^*$. This corresponds to a trimerisation of the stack. (In real systems where non-zero interstack coupling smears the perfect one-dimensional Fermi surface planes, the behaviour of the system is determined by a balance between the size of the trimerisation gap and the warpage of the Fermi surface). We find that the stacks of the ET molecules in the β phase are strongly trimerised thus reflecting the highly one-dimensional character of its crystal structure. Moreover this explains why the material is an insulator.

The structures of both the α and γ phases are much less one dimensional than the β phase and indeed we propose that the ET molecules are arranged in an optimum

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[†] Unfortunately it won't be possible to discuss in detail the large amount of data we have obtained on these materials because of limited space: we hope to describe these results elsewhere[8].

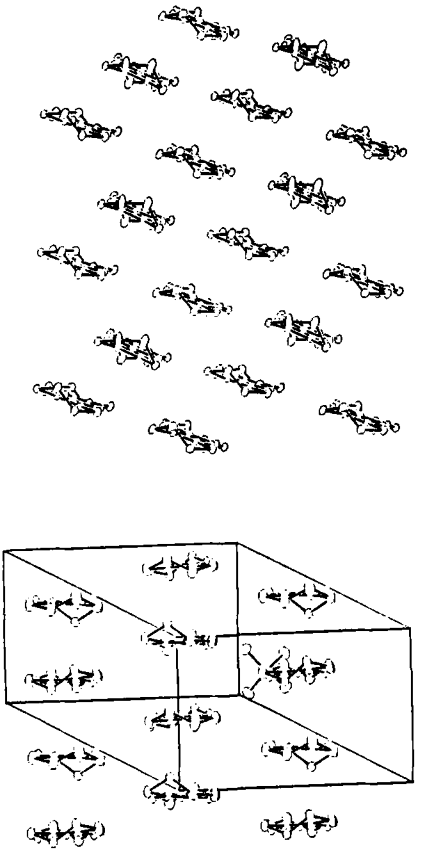

Figure 10: Comparison of the arrangement of the ET molecules in a single plane for (a) α-ET$_3$(ReO$_4$)$_2$ and (b) (ET)$_2$(ReO$_4$). Views along the long axes of the molecules are shown.

configuration for two-dimensional interactions for the α and γ phases (see Figure 10(a)). This is a result of the tilting of the ET molecules such that one ET molecule interacts with four surrounding ET molecules (note that the *side-by-side* ET molecules in figure 10(a) are situated very poorly for bonding because as discussed earlier the S-S overlap integral passes through some zero value for $\phi \simeq 20°$) The packing of the ET molecules is clearly quite different in these phases as compared with the ET$_2$X (or (TMTCF)$_2$X) structure. These are compared in figure 10. Finally note that the structure of the α phase is related to that of the δ phase exhibited by many of the ET salts containing smaller anions. There is a similar stacking of ET molecules within one plane of molecules (which is separated from adjacent molecular planes by a plane of anions) except that the unit cell contains two independent planes of molecules in the α phase but only a single plane in the δ phase. Further discussion and details of these structures are described elsewhere[6,8].

The structure of γ-$ET_3(ReO_4)_2$ is quite different from all the other phases of ET that we have so far prepared in one important respect. The ReO_4^- anions are disordered at 300K. The disorder is quite unlike that found in the $(TMTCF)_2X$ salts. In the ET salt at each anion site there are two anion positions such that the anions share one oxygen site and the central Re atoms are separated by more than 1Å There is a weak anomaly in the resistivity curve for γ $ET_3(ReO_4)_2$ shown in figure 9 near 200 K which we have seen more clearly in thermopower data. Detailed room and low temperature structures for this material show that below 200 K the unit cell is doubled in volume and the anion disorder is removed[8].

5-CONCLUSIONS

A major feature of the ET molecule is its ability to take part in a multitude of crystal phases with different charge states. We suggest that the extreme and perhaps unexpected flexibility of the outer rings of the ET molecule which can make an angle of as much as 45° with the plane of the inner portion of the molecule[8] may be an important clue towards an explanation of this phenomenon. We have shown that anions smaller than some certain size apparently stabilise a single crystallographic phase. As the anion size is increased a number of very different sets of structures are found.

We have found for the ReO_4^- anion four different crystal structures involving two different charge states of the ET molecule. We have shown that the wide variety of electronic properties of these systems can be understood by careful studies of their crystal structures. We have suggested that for the compounds of the form, $ET_3(ReO_4)_2$, the energy gap resulting from the trimerisation of the molecular stack can be washed out to a varying degree by inter-stack interactions which increase the effective dimensionality of the system. We have emphasized that a consideration of the dimensionality of such systems in terms of chemical bond lengths without taking into account bond angles is simple-minded and misleading. The overlap integral for such bonds is far more sensitive to bond angle than it is to bond length and can be negligibly small for certain bond angles.

We started out our work on ET salts with the hope of finding many new organic superconductors. These hopes have largely been frustrated and superconductivity continues to remain elusive in these and other organic charge transfer salts. This work suggests that a successful search for new superconductors in the ET family must begin with anions comparable in size to the ReO_4^- anion. Much smaller or larger anions apparently stabilise unfavourable crystal structures.

The many faces of ET will eventually provide a lengthy case history sufficient for many different and detailed diagnoses. Whether or not the schizoid behaviour of these materials can be understood and controlled remains to be seen.

ACKNOWLEDGEMENTS

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REFERENCES

1 S.S.P. Parkin *et al*, Phys. Rev. Lett. 50, 270 (1983).
2 E.B. Yagubskii, I.F. Shchegolev, V.N. Laukhin, P.A. Kononovich, M.V. Kantsovnik, A.V. Zvarykina and L.I. Buravov, JETF 39, 12 (1984).
3 G. Saito, T. Enoki, K. Toriumi and H. Inokuchi, Solid State Comm. 42, 557 (1982).
4 V. Lee, E.M. Engler, R. Schumaker and S.S.P. Parkin, J. Chem. Soc. Chem. Commun., 235 (1983).
5 For references see Proc. Conf. Synthetic Metals, Les Arcs, J. de Phys. 44-C3, (1983).
6 S.S.P. Parkin and W.A. Aiello (unpublished).
7 S.S.P. Parkin, in Proc. N.A.T.O. Davy Advanced Scientific Institute, Cambridge, edited by J.V. Acrivos (Reidel, 1984).
8 S.S.P. Parkin *et al* (to be published).
9 H. Kobayashi *et al* (these proceedings).
10 S. Oostra and S.S.P. Parkin (unpublished).
11 R. Laversanne *et al* (these proceedings).
12 S.S.P. Parkin, J.M. Mayerle and E.M. Engler, J. de Physique 44, C3-1105 (1983).
13 C. Coulon *et al*, Phys. Rev. B26, 6322 (1982).
14 L. Pauling, The Nature of the Chemical Bond (Cornell University Press, 1960)
15 P. Grant, J. de Physique 44, C3-847, (1983).
16 J. Williams *et al* (these proceedings).
17 G. Klopman and R.C. Evans, in Semiempirical Methods of Electronic Structure Calculation: Part A: Techniques, edited by G.A. Segal (Plenum, New York, 1977), p. 29.
18 R.S. Mulliken, C.A. Rieke, D. Orloff and H. Orloff, J. Chem. Phys. 17, 1248 (1949).