1 of 1

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 "Materials and Crystallographic Aspects of High T_c Superconductivity"
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STRUCTURE-PROPERTY RELATIONSHIPS IN RADICAL-CATION (ELECTRON-DONOR MOLECULE) AND ANION-BASED (INCLUDING FULLERIDES) ORGANIC SUPERCONDUCTORS AND THEIR USE IN THE DESIGN OF NEW MATERIALS

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Abstract

The presently known structure-property relationships that have been developed for organic superconductors based on the ET molecule (b-phases and k-phases), and the C_{60} -anion-based fullerides, and their use in the structural design of new superconducting materials are discussed.

Introduction

Whereas most organic substances are insulators, there is a class of conducting organic materials known as "synthetic metals" or "organic metals." Amongst the thousands of existing organic substances a very few, but steadily rising number, are superconducting at ambient pressure or under modest applied pressures.¹ The "molecular components" from which organic superconductors are derived are given in Figure 1, and a listing of these superconductors other than those derived from C_{60} is given in Table 1.

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Fig. 1. Molecular components of organic superconductors.

Table 1. Radical-cation based organic superconductors and their critical temperatures.

Compound	$T_c^\dagger$ (K)	Compound	$T_c^\dagger$ (K)
<i>TMTSF compounds</i>			
(TMTSF) ₂ PF ₆	0.9 (12 kbar)	κ -(ET) ₄ Hg _{3-3}} Cl ₈	1.8 (12 kbar); 5.3 (29 kbar)
(TMTSF) ₂ AsF ₆	1.1 (12 kbar)	κ -(ET) ₄ Hg _{2.89} Br ₈	4.3; 6.7 (3.5 kbar)
(TMTSF) ₂ SbF ₆	0.4 (11 kbar)	(ET) ₂ Hg _{1.41} Br ₄	2.0
(TMTSF) ₂ TaF ₆	1.4 (12 kbar)	α -(ET) ₂ [(NH ₄)Hg(SCN) ₄]	1.15
(TMTSF) ₂ ReO ₄	1.3 (9.5 kbar)	(ET) ₃ Cl ₂ ·2H ₂ O	2.0 (16 kbar)
(TMTSF) ₂ FSO ₃	2.1 (6.5 kbar)	κ -(ET) ₂ Cu(NCS) ₂	10.4
(TMTSF) ₂ ClO ₄	1.4	κ -(ET) ₂ Ag(CN) ₂ ·H ₂ O	5.0
<i>ET compounds</i>			
(ET) ₂ ReO ₄	2.0 (4.5 kbar)	κ -(ET) ₂ Cu[N(CN) ₂] ₂ Br	11.6
β -(ET) ₂ I ₃ ‡	1.4	κ -(ET) ₂ Cu[N(CN) ₂] ₂ Cl	12.8 (0.3 kbar)
β^* -(ET) ₂ I ₃ §	8.0 (0.5 kbar)	<i>DMET compounds</i>	
γ -(ET) ₃ (I ₃) _{2.5}	2.5	(DMET) ₂ Au(CN) ₂	0.8 (5 kbar)
θ -(ET) ₂ I ₃	3.6	(DMET) ₂ I ₃	0.47
κ -(ET) ₂ I ₃	3.6	(DMET) ₂ IBr ₂	0.59
α -(ET) ₂ I ₃	7-8	(DMET) ₂ AuCl ₂	0.83
(α/β)-(ET) ₂ I ₃	2.5-6.9	(DMET) ₂ AuI ₂	0.55 (5 kbar)
β -(ET) _{1.96} (MET) _{0.04} I ₃	4.6	(DMET) ₂ AuBr ₂	1.0 (1.5 kbar)
β -(ET) ₂ IBr ₂	2.8	κ -(DMET) ₂ AuBr ₂	1.9
β -(ET) ₂ AuI ₂	4.98	<i>Other compounds</i>	
		κ -(MDT-TTF) ₂ AuI ₂	4.5
		β_m -(BEDO-TTF) ₃ Cu ₂ (SCN) ₃	1.06
		(TTF)[Ni(dmit) ₂] ₂	1.6 (7 kbar)
		Me ₄ N[Ni(dmit) ₂] ₂	5.0 (7 kbar)
		α' -(TTF)[Pd(dmit) ₂] ₂	6.42 (20.7 kbar)
		α -(TTF)[Pd(dmit) ₂] ₂	1.7 (21.75 kbar)

†At ambient pressure in those entries where no pressure is indicated in parentheses.

‡Also referred to as β_L -(ET)₂I₃ §Also referred to as β_H -(ET)₂I₃.

The first organic superconductor, quasi-1D (TMTST)₂PF₆ ($T_c = 0.9$ K) required considerable pressure ($p = 9$ kbar) to suppress a metal-insulator antiferromagnetic ordering transition (spin density wave, SDW) that occurred at ~ 16 K.² Competition between magnetic (SDW) and superconducting ground states are often observed in organic superconductors and SDW driven transitions occur when the on-site electron-electron Coulomb repulsion exceeds the stabilization gained from delocalization. In such cases electrons are localized to reduce the Coulomb repulsion and the ground state is that of an antiferromagnetically-coupled insulator (Mott-Hubbard insulator).³ The original discovery of organic superconductors² based on TMTSF (Bechgaard salts) resulted in rapid developments in the field and, to date, organic superconductors have been derived from electron-donor molecule (non-C₆₀ based) and anion-based [M(dmit)ⁿ⁻ and C₆₀³⁻] species (Fig. 1). Only the ET and C₆₀-based systems have yielded a sufficiently large number of superconductors to allow the development of useful structure-property correlations (vide infra). The structures of these materials and these correlations, where they exist, will be the focus of this paper in so much that they can provide predictive power in the design of new superconducting organic systems.

β - and κ -phase ET-based Organic Superconductors

β -PHASE SYSTEMS

The β -(ET)₂X materials, X = triatomic and monovalent anion, are ambient-pressure superconductors with T_c 's as follows, viz., 2.8 K (X = IBr₂⁻), 4.9 K (X = AuI₂⁻) and 1.5 K (and 8 K at $p > 0.5$ kbar) for X = I₃⁻. An important feature of these systems is that they are *isostructural*, with the *linear-triatomic* anions occupying a cavity created by the ET-molecule ethylene-group hydrogen atoms formed from the "corrugated-sheet" layer-like packing of the electron-donor molecules, as shown in the stereodiagram in Fig. 2. The β -phase salts are actually *layered superconductors*, with the repeat unit being one layer of the conducting electron-donor molecules (in a general crystallographic position in the triclinic space group $P\bar{1}$, see Fig. 3) and one layer formed by the anions (located on inversion symmetry centers). In these systems the organic molecules are oriented parallel to each other and the molecular stacking axis occurs along the unit cell diagonal direction. The short S...S intermolecular contacts less than 3.6 Å, the van der Waals S...S radius sum (see Fig. 3), are formed between molecules on neighboring stacks and the resulting honeycomb network they create in β -(ET)₂X systems is the electron conduction pathway in the donor-molecule layers (the anions are insulators). The effect of varying the linear-anion length is to change the unit cell volume in the same fashion, while also altering the network system of *intra*- and *intermolecular* S...S contacts. A representative set of linear anions that yield β or β -like structures is given in Table 2, in which anion length, unit cell volume, and T_c (if appropriate) are presented.

Fig. 2. Perspective view of a single $(X-X-X)^{-}$ anion surrounded by ET molecule $-CH_2$ groups, in the H-pocket made up of 12 ET molecules in the $\beta-(ET)_2X$ structure.

Fig. 3. ET molecule networks in β - and κ -type organic superconductors. Thin lines indicate short intermolecular S...S contacts, and the unit cell boundaries are also indicated by faint lines.

Table 2. β -(ET) $_2$ X Salts (Anions and Properties)

X		Anion Length (Å)	V_a (Å ³ at 298 K)	T_c (K)
I_3^-		10.1	855.9	1.5
AuI_2^-		9.4	845.2	5
I_2Br^-		9.7	842.3	none
IBr_2^-		9.4	828.7	2.80
$ClIBr^-$		9.0	821.3	?
ICl_2^-		8.7	814.3	$T_{MI} = 22.1$
$AuCl_2^-$		8.1	800.7	$T_{MI} \approx 32$

It is noteworthy that for the shortest anions, i.e., ICl_2^- and $AuCl_2^-$ the salts undergo metal-insulator transitions below 40 K and the structures are only β -like due to the distortions of the regular β -lattice arising from $Cl \cdots H$ and anion-ET molecule interactions. It is important to further point out that anion-donor molecule contacts in the ET-anion systems are through weak $-CH_2 \cdots X$ (X = halide) hydrogen bonding interactions, and it is known the T_c 's of the superconducting β -salts increase as these interactions increase in "softness"¹ of these contacts as longer anions are used due to an increase in electron-phonon coupling constants (λ) in agreement with BCS theory. Softness increases as the length of the anion is increased due to a weakening of hydrogen bonding $-CH_2 \cdots X$ interactions as the atomic number and electronegativity of the halogen (X) increases, and also from a similar lengthening of the $S \cdots S$ contacts between ET molecules that parallels the increase in anion length. While the *centrosymmetric* anions (I_3^- , AuI_2^- , and IBr_2^-) provide ambient pressure superconductors, the *unsymmetric* I_2Br^- and $ClIBr^-$ anions produce nonsuperconducting products due to the disorder they induce in the lattice by random occupation of the crystallographic center of symmetry, which increases electron scattering and inhibits Cooper-pair formation. Again, β -(ET) $_2I_3$ is novel because a slight pressure of only 0.5 kbar⁴ is sufficient to convert it from a modulated structure (below ~ 175 K, $T_c = 1.5$ K) to a fully ordered structure [β^* -(ET) $_2I_3$, $T_c = 8$ K]⁵ which has the highest T_c found in the β -phase organic superconductors. The three isostructural and centrosymmetric linear-anion salts (I_3^- , AuI_2^- and IBr_2^-) form the basis of a structure-property correlation that suggests T_c 's as high as 40 K might result from the use of complex anions such as $(NCS-M-SCN)^-$, $(NCSe-M-SeCN)^-$, M = metal, etc., if they could be synthesized, were linear and could be incorporated into the β -(ET) $_2X$ structure (see Fig. 4).

Fig. 4. Correlation of linear anion length in $\beta\text{-(ET)}_2\text{X}$ salts with superconducting critical temperature T_c and possible new anionic derivatives with higher T_c 's.

Finally, in the β -phase superconductors, the dependence of T_c on X^- and pressure⁶ (p) is also related to changes in the lattice softness¹ as a function of X^- and p , and a plot of T_c vs. p is given in Figure 5.

Fig. 5. Pressure dependence of the T_c of $\beta\text{-(ET)}_2\text{X}$ ($\text{X}^- = \text{I}_3^-, \text{AuI}_2^-, \text{IBr}_2^-$).

κ -PHASE SYSTEMS

Another important type of molecular packing motif occurs in the " κ -phase" ET-based materials, which contain orthogonally oriented ET-molecule dimers (see Fig. 3) and form layered superconductors possessing alternating layers of radical-cations and anions (the anions may be polymeric, see Fig. 6).

Fig. 6. Layered structure of κ -phase organic superconductors.

The resulting superconductors have T_c 's as high as 12.8 K (the maximum presently observed for radical-cation systems). Attempts to prepare β -phase salts with the $X = \text{"Cu(NCS)}_2^- \text{"}$ (see Fig. 4) anion led to the first superconducting ET salt with a $T_c > 10$ K, but with a κ -phase, rather than β -packing motif. Furthermore, the $\text{"Cu(SCN)}_2^- \text{"}$ anion is *not* linear, but is trigonal and *polymeric*.⁷ In fact, the highest T_c 's observed in the ET-based superconductors are found in κ -phase systems containing "self-assembling" polymeric anions derived from complexes of Cu^+ (vide infra).

The κ -(ET) $_2$ Cu(NCS) $_2$ salt was unusual due to the presence of a polymeric anion derived from a trigonally coordinated Cu^+ ion. While attempting to prepare substituted salts of Cu^+ and the dicyanamide $[\text{N(CN)}_2]^-$ anion in place of $(\text{SCN})^-$, three novel κ -phase derivatives, again containing polymeric anions (see Fig. 7),^{8,9} were discovered, viz., κ -(ET) $_2$ Cu[N(CN) $_2$]X, $X = \text{Cl}^-$, Br^- and I^- . The $X = \text{Br}^-$ and Cl^- salts exhibit the highest T_c 's discovered in radical-cation based organic superconductors¹ whereas, surprisingly, the I^- derivative is a semiconductor. More importantly, even although these salts are *isostructural* they differ considerably in their electrical properties, i.e., the Br-salt⁸ is an ambient pressure superconductor with $T_c = 11.6$ K, the Cl-salt⁹ becomes superconducting ($T_c = 12.8$ K, the highest T_c found in any ET-based superconductor) under the smallest pressure (0.3 kbar) required to suppress a SDW transition for any organic superconductor. Furthermore, magnetization measurements at ambient pressure of the Cl^- salt reveal an antiferromagnetic transition near 45 K and, *for the first time in this class of materials*, a transition near 22 K to a state exhibiting weak ferromagnetic hysteresis effects.¹⁰

Fig. 7. $\text{Cu}[\text{N}(\text{CN})_2]\text{X}^-$ anions $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{X}$, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$.

Calculations revealed that the band structures of the three $\text{Cu}[\text{N}(\text{CN})_2]\text{X}^-$ salts are virtually the same and do not account for the differences in the observed electrical properties.¹ The principal structural difference between the superconducting $\text{Cu}[\text{N}(\text{CN})_2]\text{X}$, $\text{X} = \text{Cl}^-, \text{Br}^-$ salts, and the semiconducting $\text{X} = \text{I}^-$ derivative, is that whereas the former are crystallographically *ordered* at low temperatures, the $\text{X} = \text{I}^-$ salt (which is not superconducting at $p < 5$ kbar) is not due to the presence of ET-molecule $-\text{CH}_2$ -group disorder even at 16 K.¹ An analysis based on the "lattice softness" concept,¹ which arises from short intermolecular $\text{C-H}\cdots\text{anion}$ and $\text{C-H}\cdots\text{H}$ contacts in both the β - and κ -phase systems and its relationship to T_c , has also been applied to the $\text{Cu}[\text{N}(\text{CN})_2]\text{X}$, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ salts with limited success.¹¹ Finally, future anionic substitution reactions on trigonal Cu^+ ions may continue to provide new κ -phase derivatives with unusual electrical properties.

Attempts to develop structure-property relationships for the superconducting κ -phase derivatives of ET have proven difficult, yet a first attempt at an empirical correlation is shown in Figure 8 by use of the data listed in Table 3.

Fig 8. T_c vs. V_c for κ -phase ET salts.

Table 3. The unit cell constants and T_c 's for κ -(ET)₂X salts.

Compound	a (Å)	b (Å)	c (Å)	T_c (K)	Volume (Å ³)
CuN(CN) ₂ I*	12.960	8.680	30.340	-	1706.0
Cu(NCS) ₂	13.143	8.456	16.256	10.4	1694.8
CuN(CN) ₂ Br*	12.942	8.539	30.016	11.6	1658.5
CuN(CN) ₂ Cl *	12.977	8.480	29.979	12.5	1649.5
Ag(CN) ₂ (H ₂ O)	12.593	8.642	16.080	5.00	1651.2
I ₃	12.832	8.466	16.387	3.60	1687.6
Hg ₃ Br ₈ *	11.219	8.706	37.105	6.70	1812.0
Hg ₃ Cl ₈ *	11.062	8.754	35.920	5.30	1739.0
Cu ₂ (CN) ₃	13.400	8.586	16.117	2.80	1701.2
Cu ₂ (CN) ₃₋₄ Br ₄	13.400	8.590	16.250	2.60	1710.0
Cu[N(CN) ₂]CN	12.887	8.647	15.987	10.7	1664.0
Cu[N(CN) ₂]CN	13.324	8.543	16.093	3.80	1687.0

*The volume listed = $\frac{\text{real volume}}{2}$ because they contain double layer structures.

In the κ -phases there appear to be separate correlations for different anion configurations based on either structurally 1-D anion (zig-zag) chains, such as found in Cu[N(CN)₂]X⁻ salts (top line, Fig. 8), or structurally 2-D anion layers (2-D networks) in salts such as that observed in κ -(ET)₂I₃ (bottom line, Fig. 8). However, in surprising contrast to the β -(ET)₂X series, T_c *increases*, rather than decreases, with *decreasing* unit cell volume. The basis of these empirical relationships is

under intense study currently and a better understanding of their origin is required before rational design criteria can be developed for κ -phase materials. Finally, based on years of experience gained by various investigators world-wide, the radical-cation (ET, etc.) superconductors are air-stable over long periods of time (years). However, they are brittle materials and not readily amenable to mechanical bending and forming.

C₆₀-based Organic Superconductors

In distinct contrast to the nearly planar radical-cations derived from the ET molecule and similar electron-donor molecules given in Fig. 1, are the remarkable new superconductors derived from the essentially *spherical* and all carbon-containing electron-accepting buckminsterfullerene molecule, C₆₀. Whereas the ET-based systems are usually 2D and of low symmetry (triclinic), the M₃C₆₀, M = alkali metal, organic superconductors are derived from the packing of spherical species (M⁺ and C₆₀³⁻) to form cubic (isotropic) structures and, therefore are truly 3D conductors. In addition, the T_c's of the fullerides are substantially higher (~33 K in Rb₂CsC₆₀) than those presently known for the ET-based superconductors (present maximum 12.8 K). Table 4 contains a list of relevant unit cell data and T_c's for the FCC (face centered cubic) alkali metal-based superconductors derived from C₆₀³⁻. Based on existing data, it appears that no superconductors have been derived from purely Li or Na alone whereas pure and alloyed materials can be prepared by use of K, Rb or Cs.

Table 4. Unit cell and T_c's for FCC M_xC₆₀ salts (from D. W. Murphy, et al.).¹²

	Lattice parameter(s) (Å)	T _c (K) (%)†
Na ₂ C ₆₀ ‡	14.189 (1)	—
Na ₃ C ₆₀	14.183 (3)	—
Na ₄ C ₆₀	14.380 (8)	—
Na ₂ KC ₆₀	14.120 (4)	—
Na ₂ RbC ₆₀	14.091 (6)	—
Na ₂ Rb _{0.5} Cs _{0.5} C ₆₀	14.148 (3)	8.0 (3)
Na ₂ CsC ₆₀ No. 1§	14.132 (2)	10.5 (8)
Na ₂ CsC ₆₀ No. 2§	14.176 (9)	14.0 (9)
K ₃ C ₆₀	14.253 (3)	19.3 (30)
K ₂ RbC ₆₀	14.299 (2)	21.8 (32)
Rb ₂ KC ₆₀ No. 1§	14.336 (1)	24.4 (34)
Rb ₂ KC ₆₀ No. 2§	14.364 (5)	26.4 (32)
Rb ₃ C ₆₀	14.436 (2)	29.4 (35)
Rb ₂ CsC ₆₀	14.493 (2)	31.3 (48)

†T_cs and shielding fractions (%) were measured by d.c. magnetization.

‡Sample is simple cubic.

§Samples labeled No. 1 and No. 2 have the same nominal composition.

The structures of the M₃C₆₀ salts are described as intercalation compounds of the FCC structure derived from C₆₀ itself, or hypothetical BCC (body centered cubic) or BCT (body centered tetragonal) structures (vide infra).¹² For the FCC structures the octahedral and tetrahedral interstices are located on special positions in the space group with the octahedral site being *larger* than any alkali metal ion whereas the tetrahedral site most closely resembles Na⁺ in size. The C₆₀ structure and that of different M_x⁺C₆₀ⁿ⁻ materials, including the M₃C₆₀ superconductors, are shown in Figure 9.

Fig. 9. Schematic structures of C_{60} and $A_x C_{60}$ with C_{60} 's as large spheres and A as the smaller spheres. (a) FCC C_{60} drawn in an equivalent BCT representation. (b) The structure of $Na_2 C_{60}$ with Na ions in tetrahedral interstices. (c) $A_3 C_{60}$ with A ions in both tetrahedral and octahedral interstices. (d) The $A_4 C_{60}$ structure exhibited by K, Rb and Cs. (e) The FCC $A_6 C_{60}$ structure (A = Na, Ca) with the darker Na atom sites 50% occupied. (f) The BCC $A_6 C_{60}$ structure of K, Rb and Cs. (From D. W. Murphy, et al.).¹²

From a detailed analysis of the salts of C_{60}^{n-} , the structures they adopt agree with those one would predict on the basis of ion size (M^+ and C_{60}^{n-}) and from electrostatic calculations.¹² Since the $M_3 C_{60}$ salts are isostructural, the T_c 's scale with cation volume and unit cell size (see Fig. 10).

Fig. 10. Superconducting T_c 's plotted against calculated cation volume for A_3C_{60} (from D. W. Murphy, et al.).¹²

One of the surprising structural contrasts between the ET and M_3C_{60} salts is that structural disorder in the former systems either reduces T_c or destroys superconductivity altogether (e.g., β -(ET) $_2$ I $_2$ Br),¹ whereas the octahedral and tetrahedral sites of the alkali metal ions, and the C_{60}^{3-} spheres themselves, are highly disordered in the M_3C_{60} superconductors. However, one structural feature common to both ET and C_{60} -based systems is that up to a certain point the T_c 's increase steadily as either the ET-molecules, or the C_{60}^{3-} spheres, are increased in separation, i.e., as molecular overlap is reduced and, for example, as the interball C_{60} - C_{60} interactions soften. This argues for a BCS mechanism for the electron-pairing interaction in which the electronic density of states at the Fermi surface, which scales with T_c , increases as molecular overlap is decreased in these organic systems. However, the mechanism of superconductivity in organic superconductors remains an intensely studied mystery at this time!

Finally, one last important note is that the T_c 's of the superconducting organic systems are rising at a rapid rate suggesting that they may rival those of the ceramic copper-oxide systems within this decade (see Fig. 11).

Fig. 11. T_c vs year.

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10 / 18 / 93

END