

Correlation of Electrical Conductivity in Charge-Transfer Complexes with Redox Potentials, Steric Factors, and Heavy Atom Effects

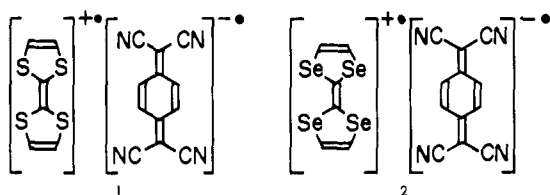
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Abstract: Electrical conductivity in charge-transfer complexes has been correlated with structure. High room-temperature electrical conductivity is associated with moderately strong electron acceptors ($-0.02 \leq E_{1A} \leq 0.35$ V), moderately strong electron donors ($0.1 \text{ V} \leq E_{1D} \leq 0.4$ V), closely matched redox potentials ($|E_{1A} - E_{1D}| \leq 0.25$ V), closely matched donor and acceptor molecular dimensions, and the introduction of heavy atoms. Heavy atoms, however, do not seem to have a direct effect on the maximum enhancement in conductivity observed on lowering temperature. But of seven complexes showing metallic electrical conductivity, the magnitude of conductivity enhancement correlates with the semiconductor transition temperature. Conductivity is decreased by bulky substituents and possibly by doping with closely related molecules. Many of these effects are rationalized in terms of crystal packing and the extent of electron transfer.

Introduction

At room temperature tetrathiofulvalene-tetracyanoquinodimethan (TTF·TCNQ) (**1**)^{1,2} and its selenium analogue **2**³ conduct electricity nearly as readily as graphite. Conductivity increases in a metallic manner on lowering temperature until maxima are reached around 60 K for **1** and 40 K for **2**.



Reported enhancements at 60 K for TTF·TCNQ have ranged from ten⁻¹ to 500⁻²fold, forming the basis for a lively debate.⁴⁻⁸ Those factors felt to have an important influence on the electrical conductivity of TTF·TCNQ and similar materials include the presence of unpaired electrons, crystal structure, degree of electron transfer, small separation between first and second redox potentials, high acceptor electron affinity, low donor ionization potential, high symmetry, high polarizability, molecular dimensions, crystalline disorder, and dopants or impurities.¹⁻¹⁷

This paper correlates the electrical conductivities of the complexes in the preceding paper²⁴ with redox potentials, heavy atom substitution, and steric factors. These are variables that the synthetic organic chemist can readily affect in the laboratory. Such variables are far removed from the bandwidths, Fermi surfaces, Peierls instabilities, and scattering processes that solid state physicists require for a satisfactory description, and it is hoped that weaknesses inherent in the translation can be forgiven. Nonetheless useful correlations with predictive value and perhaps real physical significance have been found in the language of the organic chemist. The reader should be aware that these correlations are not based on the true isolation of single variables; for example, the effect of redox potential on electrical conductivity cannot be studied without superimposed effects from crystal structure, polarizability, and molecular size. More than one interpretation is generally possible. The rationalizations accompanying the correlations are those models we have found most useful for directing the synthesis of highly conductive materials.

Correlation with Redox Potentials

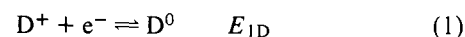
Electrical conductivity in charge-transfer complexes requires at least some electron transfer from donor to acceptor since unpaired electrons appear necessary for electron mobility. This does not necessarily mean, however, that full electron transfer generating the maximum number of unpaired electrons particularly favors conductivity. Indeed, it has been known for some time that "complex salts" which may be considered examples of partial electron transfer are frequently more conductive than their corresponding full electron-transfer "simple



salts".^{12,13,18} As a specific case, "complex salt" **3** with an average $\frac{1}{2}$ unpaired electron per TCNQ has formally 50% electron transfer, while "simple salt" **4** with one unpaired electron per TCNQ has formally 100% electron transfer. Salt **3** is roughly 10⁹ as conductive as **4**.¹² Such higher conductivity in "complex salts" over "simple salts" has been rationalized in terms of decreased electron-electron repulsion since there are a greater number of sites per electron in "complex salts".^{9,11} As an alternate explanation, salt **4** has a formally half-filled band which is particularly favorable to lattice distortions that can open a gap at the Fermi surface (i.e., Peierls instability).

The precise extent of electron transfer in TTF·TCNQ itself has remained elusive. The temperature dependence of its ESR and static paramagnetic susceptibilities^{22,23} is sufficiently complicated as to exclude estimation of unpaired electron density. Comparison of bond lengths and bond angles in neutral TTF and TCNQ to those in the complex suggests partial to full electron transfer.¹⁰ UV and x-ray photoemission spectra show the presence of both neutral and charged species with electron transfer estimated $\geq \frac{2}{3}$,¹⁹ and most recently ESCA has shown by grazing angle experiments that little charge transfer occurs at the surface but 0.5 to 1.0 electron is transferred in the bulk.^{20,21} Hypothesizing that electron transfer calculated from solution redox potentials parallels that in the solid phase, an examination of the complexes in the preceding paper was made.²⁴

The first redox potential of donor D, E_{1D} , corresponds to eq 1 and the first redox potential of acceptor A, E_{1A} , to eq 2:



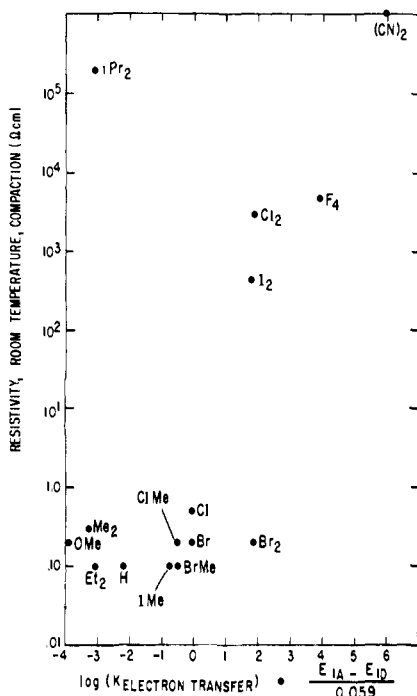
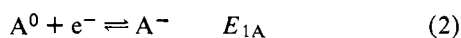


Figure 1. Resistivity vs. $\log(K_{\text{electron transfer}})$, tetrathiofulvalene complexed with substituted TCNQ's.



Their difference, $E_{1A} - E_{1D}$, is related to the equilibrium constant, K , for electron transfer by

$$\log K = \log \left[\frac{[D^+][A^-]}{[D^0][A^0]} \right] = \frac{E_{1A} - E_{1D}}{0.059} \quad (3)$$

For example, the room-temperature equilibrium constant for one-electron transfer from TTF to TCNQ in acetonitrile calculates out as $10^{-2.2}$,

$$\begin{aligned} \log K_{\text{TTF}\cdot\text{TCNQ}} &= \log \left[\frac{(\text{TTF}\cdot^+)(\text{TCNQ}\cdot^-)}{(\text{TTF})(\text{TCNQ})} \right] \\ &= \frac{0.17 - 0.30}{0.059} = -2.2 \end{aligned}$$

This agrees reasonably well with $K_{\text{TTF}\cdot\text{TCNQ}} = 10^{-2.7}$ determined from uv spectra.²⁵

Donors were complexed with a series of similar acceptors and the resulting resistivities plotted against the logarithm of the equilibrium constant for electron transfer in solution. A plot for tetrathiofulvalene complexed with substituted TCNQ's is shown in Figure 1, the complexes being identified by their TCNQ substituent pattern.²⁴ In looking for trends, the TTF·TCNQ-*i*-Pr₂ complex can probably be disregarded because the bulky isopropyl groups block crystal packing necessary for high conductivity (see below). The interesting point is that the stronger acceptors for which complete electron transfer is most likely ($K_{\text{electron transfer}} = 10^{0.2}$ to 10^6) give poorly conductive complexes, whereas the weaker electron acceptors ($K_{\text{electron transfer}} = 10^{0.2}$ to 10^{-4}) give highly conductive complexes. This is not an isolated observation since 18 substituted 1:1 TTF·TCNQ complexes²⁴ show a similar correlation.

Lowering donor strength to the point where significant electron transfer is unlikely uniformly gives poorly conductive complexes.²⁴ For example, tetramethoxyselenanthracene (TMSA) (5) first shows irreversible polarographic oxidation at $E_{\text{OX}} = 0.90$ V compared with E_{1D} of 0.30 V for TTF and

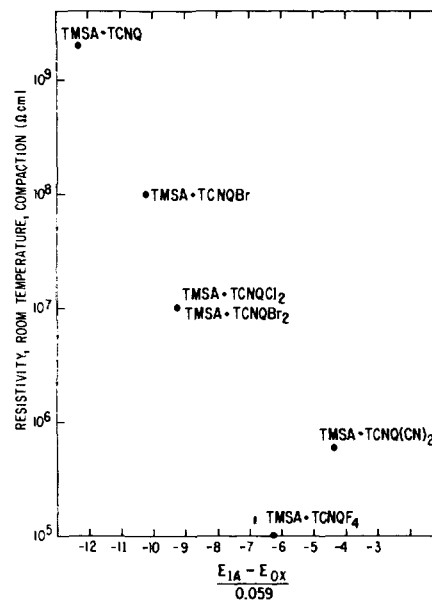
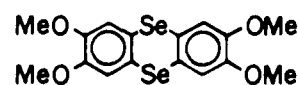


Figure 2. Resistivity vs. $(E_{1A} - E_{\text{OX}})/0.059$, tetramethoxyselenanthracene complexed with substituted TCNQ's.



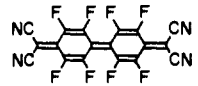
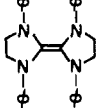
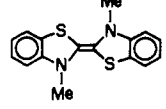
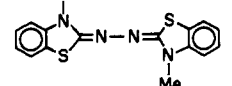
5 24; TMSA

all of its complexes have $\rho \geq 10^5 \Omega \text{ cm}$.²⁴ In spite of the small degree of electron transfer expected for these complexes, dramatic variation with acceptor strength is still seen in the plot of resistivity vs. $[E_{1A} - E_{\text{OX}}]/0.059$ in Figure 2. A speculative interpretation can be based on Figures 1 and 2. With an insignificant degree of electron transfer, as in the case of the TMSA complexes, conductivity is poor. As charge transfer increases, conductivity increases to a maximum as seen for the best TTF·TCNQ complexes. This maximum in conductivity occurs at less than full electron transfer, perhaps for the same reason "complex" salts are better conductors than "simple" salts (see above). Conductivity then again decreases as one-electron transfer is approached as in the case of "simple" salt 4 and probably of the poorly conductive TTF·TCNQ salts.

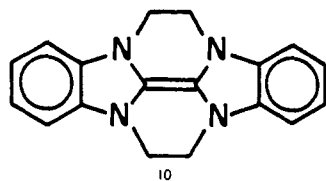
Whether or not the above interpretation is accepted, the complexes in the preceding paper²⁴ suggest the following empirical correlations. No complexes involving either extremely strong or weak donors or acceptors give highly conductive materials. Rather, high conductivity ($\rho \leq 0.1 \Omega \text{ cm}$) is associated with moderately strong acceptors ($-0.02 \text{ V} \leq E_{1A} \leq 0.35 \text{ V}$) in combination with moderately strong donors ($0.1 \text{ V} \leq E_{1D} \leq 0.4 \text{ V}$) such that redox potentials are closely matched ($|E_{1A} - E_{1D}| \leq 0.25 \text{ V}$). This correlation as well as later ones are subject to strict requirements of crystal structure. For high conductivity at least the anion or cation radical, must stack on top of itself closer than van der Waals as described in the next section. Otherwise, regardless of how favorable factors such as redox potentials are, conductivity will be poor. Chances for favorable crystal packing can probably be increased by choosing donors and acceptors without bulky substituents and of about the same overall molecular dimensions (see next section).

Garito and Heeger have argued that a small difference between first and second redox potentials, $E_1 - E_2$, favors high conductivity.⁹ Four donors and acceptors used in the previous paper have particularly small $E_1 - E_2$ differences (Table I),

Table I. Difference between First and Second Redox Potentials, $E_1 - E_2$

		$E_1 - E_2$
6		0.18 ²⁴
7		0.08 ²⁸
8		0.15 ²⁴
9		0.32 ²⁴

but they have uniformly given rather poorly conductive complexes. This is not as contradictory as it might seem for two reasons. First, all four are also among the too strong donors and acceptors that have given poor conductivity results in general. Second, all four systems are capable of nonplanarity as radical ions in solution, whereas similar systems held in a rigid planar conformation such as would be expected in a conductive crystal matrix actually have rather large $E_2 - E_1$ differences.²⁶ For example, **10** has an $E_1 - E_2$ difference of ~ 0.85 V²⁷ compared

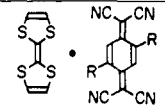


with 0.08 V in **7**, but their TCNQ complexes have very similar and poor conductivities.²⁴

Correlation with Steric Factors

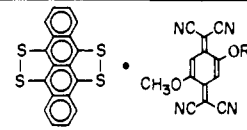
The TTF·TCNQ crystal structure consists of segregated stacks of TTF cation radicals ($\cdots D^+ \cdot D^+ \cdot D^+ \cdot D^+ \cdots$) and TCNQ anion radicals ($\cdots A^- \cdot A^- \cdot A^- \cdot A^- \cdots$).¹⁰ Both TTF and TCNQ stack face to face with considerable π overlap. The strength of this overlap is indicated by a 3.17 Å stacking distance in the TCNQ⁻ column compared with 3.45 Å in neutral TCNQ and a 3.47 Å stacking distance in the TTF⁺ column compared with 3.62 Å in neutral TTF.¹⁰ Electrical conductivity is about 1000 times as great in the direction of the columns as across them.⁴⁻⁶ Such anisotropic, "one-dimensional" conductivity has frequently been observed for stacked organic and inorganic structures and seems to most favor conductivity when the open valence shell ions are equispaced closer than their van der Waals radii.²⁹ This picture of overlapping π clouds macroscopically carrying current through a crystal is reminiscent of Little's room-temperature superconductor model¹⁵ and furthermore suggests that doping, impurities, crystal defects, substituents, or anything else that perturbs the regularity of these stacks may have a profound influence on conductivity.^{4,9,16} Two series of complexes with substituents of increasing bulk²⁴ are shown in Tables II and III. Substitution of the TCNQ moiety with increasingly large groups appears to have rather minor effect until roughly five to six side chain carbons or oxygens have been added. Beyond this point a sudden breakdown in conductivity (TTF·TCNQEt₂ →

Table II. Effect of Steric Bulk on the TTN·TCNQ System

		$\rho^{a,b}$
		
	R, -CH ₃	0.3
	R, -C ₂ H ₅	0.1
	R, -CH(CH ₃) ₂	2.10 ⁵

^a Reference 24. ^b Room-temperature compaction resistivity in Ω cm.

Table III. Effect of Steric Bulk on the TTN·TCNQ System^b

		ρ^c
		
	R, -CH ₃	0.2
	R, -C ₂ H ₅	0.8
	R, -CH(CH ₃) ₂	N.R. ^a
	R, -CH ₂ CH(CH ₃) ₂	N.R. ^a
	R, -CH ₂ CH ₂ CH(CH ₃) ₂	N.R. ^a

^a Complex fails to form on mixing trichlorobenzene solutions of donor and acceptor. ^b Note an entirely parallel result occurs in TTN complexes with dialkyl TCNQ's. TTN·TCNQMe₂, $\rho = 0.4 \Omega$ cm; TTN·TCNQEt₂, $\rho = 0.3 \Omega$ cm; TTN·TCNQ*i*-Pr₂ (N.R.); see ref 24. ^c Room-temperature compaction resistivity in Ω cm, ref 24.

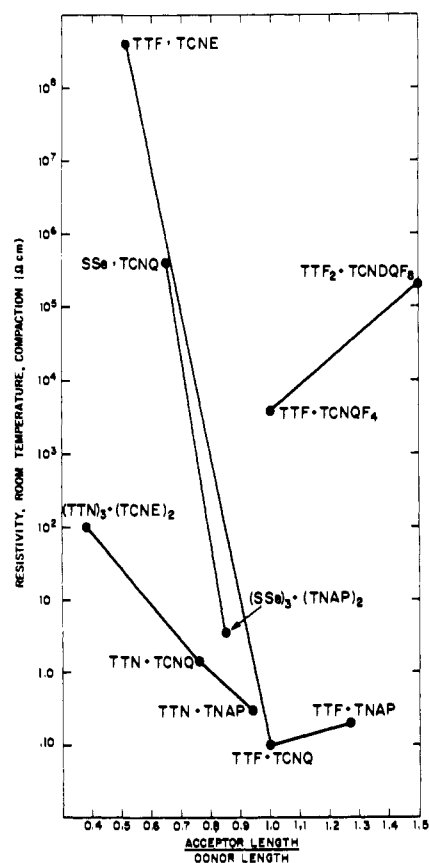


Figure 3. Resistivity vs (acceptor length)/(donor length).

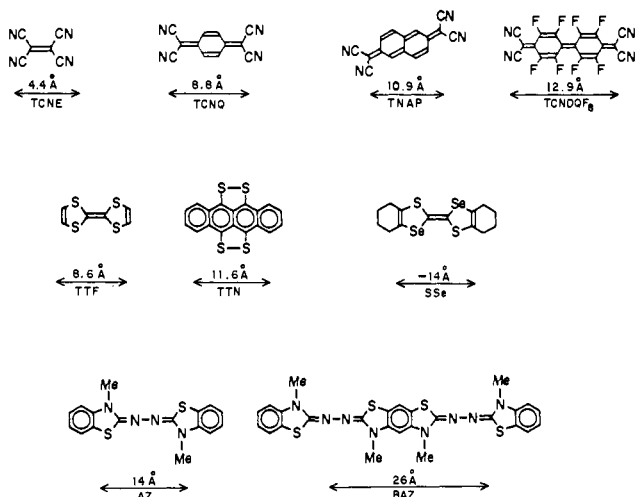
TTF·TCNQ-*i*-Pr₂) or even ability to complex [TTN·TCNQ(OMe)(OEt) → TTN·TCNQ(OMe)(O-*i*-Pr)] occurs.

The lengths of a number of the donors and acceptors used for complexation may be estimated from Dreiding models. Series of complexes holding donor constant and redox potentials reasonably steady are connected by lines in the plot of

Table IV. Heavy Atom Effects in Organic Complexes

Complex ²⁴	ρ^{24} a, b	ρ Cl complex		ρ Br complex		No. halogens
		ρ Br complex	ρ I complex	ρ I complex	ρ I complex	
TTN·TCNQCl ₂	580					
TTN·TCNQBr ₂	3	200	580	30	2	
TTN·TCNQI ₂	0.1					
TTF·TCNQCl ₂	2900					
TTF·TCNQBr ₂	0.2	15 000	65	0.004	2	
TTF·TCNQI ₂	45					
TTN·TCNQCH ₃ Cl	4					
TTN·TCNQCH ₃ Br	0.4	10	13	1	1	
TTN·TCNQCH ₃ I	0.3					
TTF·TCNQCH ₃ Cl	0.2					
TTF·TCNQCH ₃ Br	0.1	2	2	1	1	
TTF·TCNQCH ₃ I	0.1					
TTN·TCNQCl	45	4			1	
TTN·TCNQBr	12					
TTF·TCNQCl	0.5	2			1	
TTF·TCNQBr	0.2					

^a Room-temperature compaction resistivities in Ω cm. ^b Single crystal values where available²⁴ give comparable trends: $\rho(\text{TTF}\cdot\text{TCNQBr}_2)/\rho(\text{TTF}\cdot\text{TCNQI}_2) = 0.003$, $\rho(\text{TTF}\cdot\text{TCNQCH}_3\text{Cl})/\rho(\text{TTF}\cdot\text{TCNQCH}_3\text{Br}) = 17$, $\rho(\text{TTF}\cdot\text{TCNQCH}_3\text{Cl})/\rho(\text{TTF}\cdot\text{TCNQCH}_3\text{I}) = 7$, $\rho(\text{TTF}\cdot\text{TCNQCH}_3\text{Br})/\rho(\text{TTF}\cdot\text{TCNQCH}_3\text{I}) = 0.4$.



resistivity²⁴ vs. (acceptor length)/(donor length) in Figure 3. Within any particular series stoichiometry frequently varies. Thus, four separate lines are drawn connecting TTF complexed with TCNE, TCNQ, and TNAP, TTF complexed with TCNQF₄ and TCNQF₈, assorted TTN complexes, and two SSe complexes. Lowest resistivities seem to cluster near a ratio of (acceptor length)/(donor length) equal to 1. The only complexes from the preceding paper²⁴ going contrary to this trend (not shown in Figure 3) are the complexes of AZ and BAZ. The majority of the data thus suggests that mismatching of donor and acceptor sizes upsets crystal structure, lowering conductivity. Similar observations have been made by other workers.³⁰ Insufficient data is available for comment on the effect of varying molecular lengths while holding (acceptor length)/(donor length) = 1.

A number of attempts were made to dope charge-transfer complexes. For example, TTN was reacted with 3:1, 1:1, and 1:3 ratios of TCNQBrMe and TCNQBr₂ or of TCNQ and TCNQF₄. Alternatively, TTF was reacted with similar ratios of TCNQBr₂ and TCNQMe₂. In each case the TCNQ's were chosen to be about the same steric size in hopes of favoring solid solution formation over mechanical mixtures of two TCNQ salts. Finely divided powders were obtained that did not allow differentiation between mixtures and solid solutions. Nonetheless, it is interesting to note that conductivities of these powders were never significantly better and frequently worse than either of the two possible salts that would make up a

Table V. Heavy Atom Effects in Organometallic Complexes

Complex ²⁴	ρ^{24}	$\rho(\text{Pd complex})/\rho(\text{Pt complex})$
TTF ₂ ·PdS ₄ C ₄ (CN) ₄	6.10 ⁵	100
TTF ₂ ·PtS ₄ C ₄ (CN) ₄	6.10 ³	
TTN ₂ ·PdS ₄ C ₄ (CN) ₄	5.10 ³	2000
TTN ₂ ·PtS ₄ C ₄ (CN) ₄	3	

Table VI. Correlation of Conductivity Enhancement with Temperature and Heavy Atoms

Complex	Magnitude of enhancement rel to 300 K ^a	Temp at max enhancement, °K	Atoms heavier than sulfur	Ref
TTF·TCNQ, 1	17	60	None	24
TSeF·TCNQ, 2	12	40	4Se	3
TTN·TCNQ(OMe) ₂	1.9	150	None	24
TTF·TCNQEt ₂	1.4	175	None	24
TTF·TCNQICH ₃	1.3	225	I	24
TTF·TCNQClCH ₃	1.2	210	Cl	24
TTF·TCNQBrCH ₃	1.1	225	Br	24
TTF·TCNQBr ₂	1.0	275 ^b	2Br	24

^a Enhancement = 300 K/minimum; based on enhancements only in the direction of the longest crystal face and thus not necessarily the largest observable, although this is the case for solution grown TTF·TCNQ. ^b ρ 350 K/ ρ 275 K = 1.2 for TTF·TCNQBr₂.

mechanical mixture. Similarly, other workers have seen no dramatic conductivity improvements on cocrystallizing TTF·TCNQ (1) and TSeF·TCNQ (2).³² This also suggests that disturbing regular close crystal packing lowers conductivity.

Correlation with Heavy Atoms

Little's original room-temperature superconductor model,¹⁵ as well as more recent theories,^{1,2,9} have called for highly polarizable substituents close to the conductive chain or stack. Indeed the heavy atom (selenium) substituted and presumably more polarizable TSeF·TCNQ (2) appears slightly more conductive at room temperature than its sulfur analogue TTF·TCNQ (1).³ For the most part this correlation of heavy atoms with increased conductivity is seen in Table IV.³¹

There is significant improvement in conductivity on replacing chlorine with heavier and more polarizable bromine

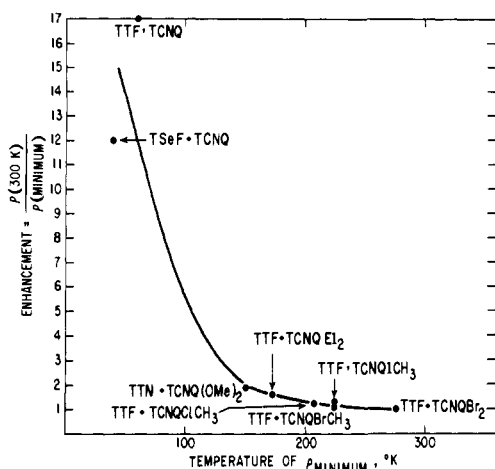


Figure 4. Enhancement vs. temperature.

and iodine. This effect is cumulative in that two bromines or iodines are more effective than one. A slight increase in conductivity at best is obtained on substituting bromine by iodine, the slight and variable direction of the change suggesting that any increase in polarizability is being offset by other factors. Similar arguments may rationalize the difference in conductivity between platinum and palladium complexes (Table V), although redox potentials vary considerably²⁴ in this case and may also be influencing the results.

Table VI compares the magnitude of conductivity enhancement on lowering temperature with the number of heavy atoms present and to the temperature at which maximum enhancement occurs. Surprisingly, while room temperature conductivity seems increased by heavy atoms, the ultimate enhancement appears relatively unaffected. More interestingly, the magnitude of enhancement appears greater the lower the temperature at which the semiconductor transition (i.e., temperature of maximum enhancement) sets in (Figure 4).

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- (31) In the context of heavy atom effects, conductivities for the sulfur analogues of $SSe\cdot TCNQ$, $SSe\cdot TCNQF_4$, and $SSe_3\cdot TNAP_2$ complexes have been reported as roughly 10^{-7} (compaction), 10^{-5} (single crystal), and 3 ($\Omega\text{ cm}$)⁻¹ (compaction), respectively, by Yamagishi, Garito, and Heeger, ref 30. Compare complexes **2-19a**, **2-19v**, and **(2)₃(20)₂** in ref 24.
- (32) *Chem. Eng. News*, **52** (39), 18 (1974).