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New Organic Synthetic Metals Derived From BEDT-TTF, Ni(dsit)₂ and
BEDO-TTF

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Abstract. Three strategies have been employed by us to synthesize new organic synthetic metals and superconductors. On the basis of structure-property correlations derived for the β -(BEDT-TTF)₂X salts, new charge transfer salts of BEDT-TTF with large, polarizable anions have been synthesized. The occurrence of molecular dimers has been engineered into salts of the new organic acceptor molecule, Ni(dsit)₂ [bis (4,5-diselenolate-1,3-dithiole-2-thione) nickelate], to synthesize salts with acceptor packing similar to the donor packing in κ -(BEDT-TTF)₂Cu(SCN)₂. Finally, two charge transfer salts of bis(ethylenedioxy)tetrathiafulvalene, BEDO-TTF, namely (BEDO-TTF)₂AuBr₂ and (BEDO-TTF)₂AuI₂ have been synthesized. The AuBr₂⁻ salt, the first BEDO-TTF salt to be structurally characterized, is semiconducting below 263 K, while the AuI₂⁻ salt shows metallic conductivity to low temperatures.

1. Introduction

Recent research on organic metals has produced an increasing number of organic superconductors. The ambient pressure superconducting transition temperatures (T_c) have risen steadily from $T_c = 1.2$ K for (TMTSF)₂ClO₄, to $T_c = 1.5, 2.8, 5.0$ K for the β -(BEDT-TTF)₂X salts where X⁻ = I₃⁻, IBr₂⁻, and AuI₂⁻ [1] respectively and to $T_c = 10.4$ K in κ -(BEDT-TTF)₂Cu(SCN)₂ [2]. In the isostructural β -phase salts, we have shown that the anion size [3] and anion-CH₂ hydrogen interactions [4,5] are critical factors that control the packing of the BEDT-TTF donor molecule and thus determine the transport properties of the resulting charge-transfer salts. Changes in the donor-to-anion "hydrogen bonding" interactions which accompany variations in anion size have been correlated to the lattice softness and phonon frequencies and, therefore, to the superconducting T_c values [5]. Thus, charge transfer salts of anions larger than I₃⁻ which retain the β -phase structure should, in principle, possess higher T_c values. An alternate approach that may be used to tailor the electrical properties of synmetals is the replacement of the BEDT-TTF donor with similar organic molecules. In this paper, we will elucidate the strategies we have employed for obtaining new synthetic metals.

2. BEDT-TTF Salts with Main Group Metal Halide Complex Anions

We have attempted to synthesize new BEDT-TTF salts with anions of the type X-M-X where M is a main group metal such as Hg, Bi, or Cd and X = Br or I in order to test the correlations between anion size and increased T_c values. The results of these experiments are not new β -phase salts with linear anions but instead salts with large complex, and sometimes polymeric, anions which force the BEDT-TTF donors into new, unusual packing arrangements.

Electrocrystallization of BEDT-TTF in the presence of BiI₃ and (n-Bu)₄NI in 1,1,2-trichloroethane (TCE) produces a 1:1 salt (BEDT-TTF)BiI₄ [6]. The crystals are triclinic, space group P $\bar{1}$, $a = 8.265(3)$, $b = 11.118(3)$, $c = 14.424(4)$ Å, $\alpha = 110.76(2)$, $\beta = 96.41(2)$, $\gamma = 103.57(2)$ °, $V_c = 1176.8(7)$ Å³, with $Z = 2$. The salt contains layers of dimerized BEDT-TTF⁺¹ cations and infinite chains of BiI₄⁻ anions. Similarly, electrocrystallization of

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BEDT-TTF in the presence of CdI_2 and $(\text{n-Bu})_4\text{NI}$ in TCE produces $(\text{BEDT-TTF})_4\text{Cd}_2\text{I}_6$ [7]. The crystals are triclinic, space group $\bar{P}\bar{1}$ $a = 8.856(7)$, $b = 11.961(9)$, $c = 18.092(11)$ Å, $\alpha = 87.72(6)$, $\beta = 84.80(6)$, $\gamma = 74.04(7)$ °, $V_c = 1835(2)$ Å³, with $Z = 1$.

Two semiconducting solvated salts [7] result from the electrocrystallization of BEDT-TTF in the presence of $[(\text{n-Bu})_4\text{N}]\text{HgBr}_3$ in TCE solvent, compound 1, $(\text{BEDT-TTF})_2(\text{HgBr}_3)(\text{TCE})$, monoclinic, $P2_1/c$, $a = 40.583(5)$, $b = 4.1830(7)$, $c = 22.766(3)$ Å, $\beta = 104.33(1)$ °, $V_c = 3744.5(9)$ Å³, $Z = 4$; and compound 2, $(\text{BEDT-TTF})_4(\text{Hg}_2\text{Br}_6)(\text{TCE})$, monoclinic, $P2_1/n$, $a = 19.344(5)$, $b = 13.401(3)$, $c = 29.418(10)$ Å, $\beta = 103.87(2)$ °, $V_c = 7404(4)$ Å³, $Z = 4$. While compound 2 contains discrete dimeric $\text{Hg}_2\text{Br}_6^{2-}$ anions, the HgBr_3^- anions in compound 1 form infinite chains. In the compound 2, eight BEDT-TTF molecules repeat along the molecular stacking axis.

While structure property correlations derived for the β -phase BEDT-TTF salts predict that large polarizable anions should give superconducting salts with higher T_c values, this prediction is based on retaining the β -phase donor packing. This is clearly not the case in the semiconducting BEDT-TTF salts with main group halide complex anions studied to date.

3. Charge Transfer Salts Derived From $\text{Ni}(\text{dsit})_2$

While the β - $(\text{BEDT-TTF})_2\text{X}$ salts contain stacks of nearly equally spaced donor molecules linked by short interstack S···S interactions, the κ -phase salts such as κ - $(\text{BEDT-TTF})_2\text{Cu}(\text{SCN})_2$ contain dimerized donor molecules which pack almost at right angles with respect to neighboring dimer pairs. The superconducting radical anion salt $\text{Me}_4\text{N}[\text{Ni}(\text{dmit})_2]_2$ ($T_c = 3.0$ K at 3.2 kbar) [8] has an acceptor packing mode similar to the β -phase BEDT-TTF salts while the semiconducting $\text{Me}_4\text{P}[\text{Ni}(\text{dmit})_2]_2$ salt contains dimeric acceptor molecules and exhibits κ -phase packing. The occurrence of dimeric acceptor molecules can be engineered into the Ni dithiolate acceptor by replacement of the inner S atoms of the dmit with Se atoms [9]. The central Ni atoms are pyramidal coordinated by five Se atoms so that the acceptor molecules form dimers in which the $\text{Ni}(\text{dsit})_2$ [bis(4,5-diselenolate-1,3-dithiole-2-thione) nickelate] molecules are linked by short Ni-Se bonds. Replacement of the inner sulfur atoms in $\text{Ni}(\text{dmit})_2$ with larger and more polarizable selenium atoms is also expected to increase the

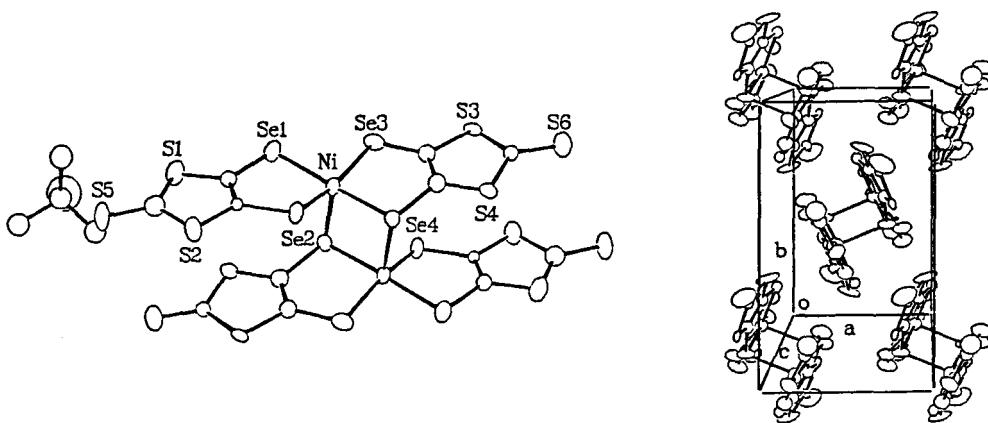


Fig. 1. Dimerization of the $\text{Ni}(\text{dsit})_2$ acceptors (left). The κ -like packing (right) in the 1:2 salts is similar to that previously reported in $\text{Me}_4\text{P}[\text{Ni}(\text{dmit})_2]_2$.

orbital overlap between molecules in the solid state and hence result in larger bandwidths. Three charge transfer salts derived from the $\text{Ni}(\text{dsit})_2$ acceptor molecule have been synthesized: two isostructural 1:2 salts $(\text{Me}_4\text{N})[\text{Ni}(\text{dsit})_2]_2$ and $(\text{Me}_4\text{P})[\text{Ni}(\text{dsit})_2]_2$ which crystallize in the orthorhombic space group Pbnm , $a = 7.409(7)$, $b = 11.875(8)$, $c = 38.32(3)$ Å, and $V_c = 3372(4)$ Å³ and $a = 7.418(5)$, $b = 11.942(9)$, $c = 38.5(1)$ Å, and $V_c = 3408(12)$ Å³, respectively; and the 1:1 salt, $(\text{Et}_4\text{N})\text{Ni}(\text{dsit})_2$, which is monoclinic, $\text{P}2_1/c$, $a = 6.775(5)$, $b = 27.02(2)$, $c = 12.973(8)$ Å, $\beta = 98.09(4)^\circ$, $V_c = 2351(3)$ Å³. Electrical conductivity and single crystal ESR measurements show that all these salts exhibit semiconducting behavior.

4. Charge Transfer Salts Derived from BEDO-TTF

Bis(ethylenedioxy)tetrathiafulvalene, or simply BEDO-TTF, has yielded several conducting charge transfer salts [10]. We report here the conductivity and structure of a new salt, $(\text{BEDO-TTF})_2\text{AuBr}_2$ which crystallizes in the monoclinic space group $\text{P}2_1/m$, $Z=2$, with unit cell parameters $a = 5.308(2)$, $b = 32.47(1)$, $c = 8.165(6)$ Å, $\beta = 98.47(5)^\circ$, and $V_c = 1392(1)$ Å³.

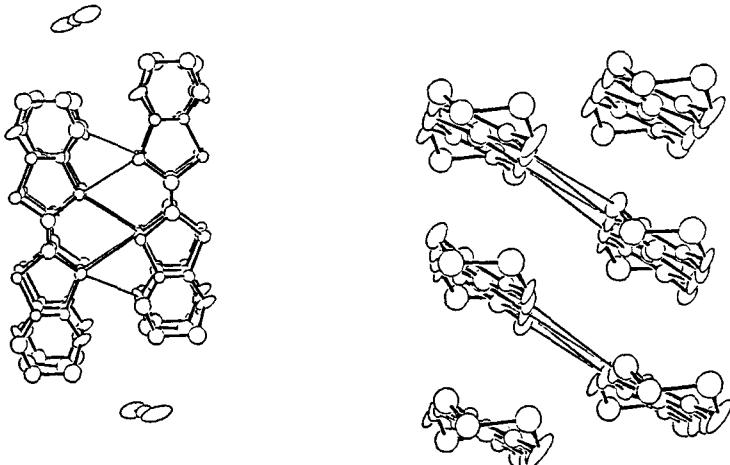


Fig. 2. The BEDO-TTF donor stacks are connected by short (less than the van der Waals sum) intermolecular $\text{S}\cdots\text{S}$ and $\text{S}\cdots\text{O}$ contacts.

The unit cell contains two AuBr_2^- anions located on a crystallographic mirror plane and four BEDO-TTF molecules. The two independent BEDO-TTF donor molecules, which are located with the central carbon-carbon double bond on an inversion center, are related by non-crystallographic symmetry ($x, y, z+1/2$). Since all of the BEDO-TTF molecules are located on inversion centers, the stacks of donor molecules are equally spaced.

Preliminary x-ray crystallographic studies on salts derived from the BEDO-TTF donor and the AuI_2^- anion suggest that the poorly formed, tree-like crystals grown by electrocrystallization in TCE or THF are isostructural to the AuBr_2^- salt. Four-probe resistivity measurements on these twisted, twinned crystals shows that $(\text{BEDO-TTF})_2\text{AuI}_2$ remains metallic down to 14 K. RF penetration depth measurements on polycrystalline samples of $(\text{BEDO-TTF})_2\text{AuI}_2$ and $(\text{BEDO-TTF})_2\text{AuBr}_2$ show that neither salt exhibits superconductivity down to 0.55 K at ambient pressure.

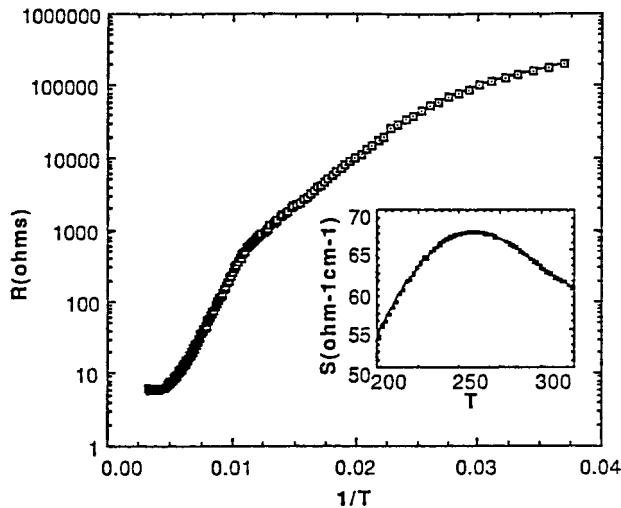


Fig. 3. Four probe resistivity measurements on single crystals of $(BEDO-TTF)_2AuBr_2$ show that this salt is metallic down ~ 263 K. At lower temperatures, semiconducting behavior is observed. The semiconducting gap is 0.12 eV (220 - 80K).

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5. Literature References

1. J. M. Williams, H. H. Wang, T. J. Emge, U. Geiser, M. A. Beno, P. C. W. Leung, K. D. Carlson, R. J. Thorn, A. J. Schultz, M. H. Whangbo: in S. Lippard (ed.), *Prog. Inorg. Chem.*, Vol. 35 (John Wiley and Sons, New York, 1987) p.p. 51-218.
2. H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, J. Tanaka: *Chem. Lett.* **1988**, 55 (1988).
3. T. J. Emge, P. C. W. Leung, M. A. Beno, H. H. Wang, M. A. Firestone, K. S. Webb, K. D. Carlson, J. M. Williams, E. L. Venturini, L. J. Azevedo, J. E. Schirber: *Mol. Cryst. Liq. Cryst.* **132**, 363 (1986).
4. P. C. W. Leung, T. J. Emge, M. A. Beno, H. H. Wang, J. M. Williams, V. Petricek, P. Coppens: *J. Amer. Chem. Soc.* **107**, 6184 (1985).
5. M.-H. Whangbo, J. M. Williams, A. J. Schultz, T. J. Emge, M. A. Beno: *J. Amer. Chem. Soc.* **109**, 90 (1987).
6. U. Geiser, H. H. Wang, S. M. Budz, M. J. Lowry, J. M. Williams: *Inorg. Chem.* submitted for publication.
7. U. Geiser, H. H. Wang, J. M. Williams: in preparation.
8. A. Kobayashi, H. Kim, Y. Sasaki, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, W. Sasaki: *Chem. Lett.* **1987**, 1819 (1987).
9. P. J. Nigrey: *Synthetic Met.* **27**, B365 (1988).
10. T. Suzuki, H. Yamochi, G. Srdanov, K. Hinkelmann, F. Wudl: *J. Amer. Chem. Soc.* **111**, 3108 (1989).

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