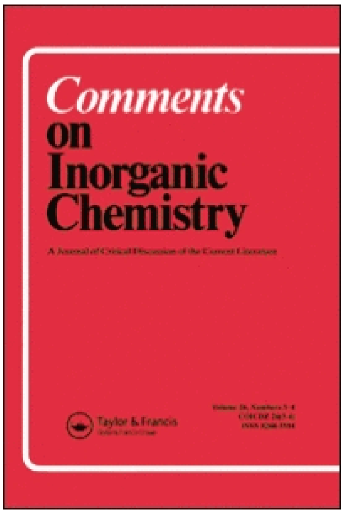

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Novel Solid State Materials Derived from Transition Metal Bis-dithiolene Complexes

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The transition metal bis-dithiolene complexes ($MS_4C_4X_4$) can be used as acceptor molecules in π-donor–acceptor-type compounds, or as radical anions in mixed valence compounds. These compounds are in the wide middle ground between the strictly organic or inorganic molecular solids on which extensive research has led to the discovery of molecular superconductors and to the development of new materials and concepts. Novel solid state materials derived from metal bis-dithiolene complexes also exhibit interesting original physical properties. In the $(TTF)[MS_4C_4(CF_3)_4]$ series of compounds, depending on the nature of the metal ion, a wide range of novel magnetic phenomena ranging from bulk ferrimagnetism (M = Ni) to spin-Peierls transition (M = Cu and Au) have been observed. Metal bis-dithiolene complexes have also been used for preparing molecular superconductors such as $(TTF)[M(dmit)_2]_2$ and $(Me4N)_{0.5}[Ni(dmit)_2]$ ($dmit^{2-}$ = 1,3-dithiol-2-thione-4,5-dithiolate) in which the conduction mechanisms are quite different from those of the strictly organic molecular superconductors.

Key Words: *transition metal bis-dithiolene complexes, novel solid state materials, spin-Peierls transition, molecular conductors and superconductors*

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INTRODUCTION

The ongoing search for new high temperature superconductors has been directly or indirectly responsible for much progress in organic and inorganic solid state chemistry. In the case of molecular solids, this research has led not only to the identification of new superconductors, but to the development of an entire class of new materials and concepts that have irreversibly transformed the study of the organic solid state.

Several recent reviews have described the progress made in this area in the case of the organic metals and superconductors on the one hand[1] and the one-dimensional inorganic conductors on the other.[2] This Comment focuses on the wide middle ground between the strictly organic and inorganic molecular solids where a unique group of metal complexes either replaces the protypical organic π-acceptor TCNQ[3] in π-donor–acceptor-type compounds, or plays the role of a radical anion in mixed valence compounds.

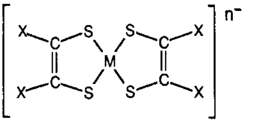
BACKGROUND

Following on the suggestion of W. Little regarding the possibility of room temperature superconductivity in quasi-"one-dimensional" molecular solids,[4] two main lines of research developed in the search for prospective molecular superconductors. One of these centered on the transition metal complexes of Pt, Ir, etc. which form 1-D chains of metal atoms in the solid state through columnar stacking of the constituent planar molecular (or ionic) units. Examples include $K_2Pt(CN)_4Br_{0.3}.3H_2O$ (KCP),[2] bis(oxalato)platinate salts,[5] and linear chain iridium complexes.[6]

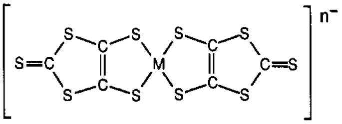
The main interaction pathway in these cases is through metal-based molecular orbitals and, in particular, the axially directed metal d_{z^2} orbital of the constituent square-planar d^8-Pt(II) or Ir(I) complexes. Partial oxidation with halogen or oxygen is generally used to generate a partially occupied conduction band and certain metal-like properties are exhibited. However, the 1-D nature of the conduction band system in these solids leads to Peierls instabilities[7] and transitions to insulating behavior as the temperature is lowered.

The parallel development of the organic metal systems, which began in earnest with the discovery of TTF-TCNQ[3] in 1973,[8] has proven to be much more fruitful in terms of novel electrical properties, leading eventually to the discovery of the first organic superconductor in 1980, $(TMTSF)_2PF_6$.[9] In this case the extended π-electron systems of the constituent planar molecular units replace the metal d_z2 orbital of the "metal-chain" complexes and both the range of possible molecules and the directionality of the interactions are much less restricted in scope.

Certain metal complexes, such as the bis-dithiolenes and phthalocyanines, by virtue of their planar molecular structure and extended π-molecular orbital system, share with the purely organic molecular systems like TCNQ and TTF the capacity for electronically significant, intermolecular, π-orbital interactions in the solid state. The phthalocyanines, in particular, have been extensively studied as metal complex alternatives to the purely organic molecular conductors.[10] In the case of the bis-dithiolene metal complexes $MS_4C_4X_4$ (MBDT) (**1**) the LUMO and HOMO are extensively delocalized over both the metal and ligands and the neutral Ni, Pd, and Pt complexes are closely related to TCNQ both in terms of their ground state electronic configuration and their capacity for reversible electron transfer reactions that yield stable anion radical species.[11]



(**1**)



(**2**)

In this case, however, the redox potentials can be readily "tuned" over a large range by variation of the ligand substituents. Moreover, changes in the metal from the Ni group to the Cu group, for example, can be effected which lead to variation in the filling of the molecular orbitals without change in the overall charge on the species. This capacity of the MBDT complexes for systematic variation in electronic structure and redox properties has been extensively exploited by our two groups in Schenectady/Troy and Toulouse in the generation of molecular solid state systems with novel electrical and magnetic properties.

By analogy to TCNQ, the MBDT complexes can potentially be used to form both mixed-valence-type complexes which contain fractional oxidation state species of the type, $[\mathrm{MBDT}]^{n-}$ (where $0 < n < 1$), in combination with a positively charged counterion, and π-donor–acceptor (or charge-transfer) compounds which combine the MBDT complex as a π-acceptor with a π-donor such as TTF. Initial efforts to obtain compounds of the former type using the substituted ethylenedithiolene complexes (**1**), proved unsuccessful,[12–14] although eventually work by Underhill and co-workers on $[\mathrm{MS_4C_4(CN)_4}]^{n-}$ complexes with small inorganic counterions such as $\mathrm{Li^+}$ did lead to the successful preparation of mixed valence MBDT complexes with quasi-metallic electrical properties.[15] As will be described later in this account, the development of the $[\mathrm{M(dmit)_2}]^{n-}$ complexes ($\mathrm{dmit^{2-}}$ = 1,3-dithiol-2-thione-4,5-dithiolate) (**2**) has advanced this phase of the research on metal dithiolene-based molecular solids considerably.

The second approach to the generation of novel dithiolene-based molecular solids, involving charge-transfer interactions with π-donors such as TTF, has also proven successful, as is evidenced by the discovery of the first example of a metal complex-based superconductor as well as a new class of quasi-one-dimensional magnetic materials, including the first "spin-Peierls" compounds. The results of these studies are described in the following sections.

COMBINATION OF THE MBDT COMPLEXES WITH ORGANIC π-DONORS

Our studies of the MBDT complexes, $\mathrm{MS_4C_4X_4}$ (**1**), as π-acceptors have focused on the X = H and $\mathrm{CF_3}$ compounds. The availability of the neutral forms of these complexes, their widely different redox properties, and the possibility of electronic structure modification through changes in the metal has provided a unique opportunity to explore structure/property relationships in π-donor–acceptor compounds.

In the case of X = H, the reduction potentials of the neutral $\mathrm{MS_4C_4X_4}$ complexes (0.09 V vs. SCE) are close to that of TCNQ

(0.13 V) and relative to TTF ($E^0(TTF^+)$ = 0.33 V) these complexes are insufficiently strong oxidizing agents to effect appreciable electron transfer in solution. On concentration and cooling, two different types of crystals were isolated, corresponding to two distinct phases with different ratios of TTF to $NiS_4C_4H_4$. Both phases are semiconductors with room temperature conductivities in the range 10^{-7}–10^{-2} S/cm.[16]

These two compounds, $(TTF)_2[NiS_4C_4H_4]$ and $(TTF)_2[NiS_4C_4H_4]_3$, have widely different structures and charge-transfer characteristics. The structure of $(TTF)_2[NiS_4C_4H_4]_3$ is particularily noteworthy. Both the diamagnetism and the structure of this compound indicates that it is comprised of neutral TTF and $NiS_4C_4H_4$ species. The structure is that of a disordered solid solution in which each molecular site in the structure can be occupied by either of the two molecules (Fig. 1).[17] The "molecule" in the average structure is thus a superimposition of the two nearly identical neutral molecules, with 0.6 Ni at the center and a pair of 0.4 C atoms close by. The outer carbon, sulfur and hydrogen atoms occur at essentially the same positions in the molecular structures of the two neutral molecules. Therefore, the remainder of the "average" mol-

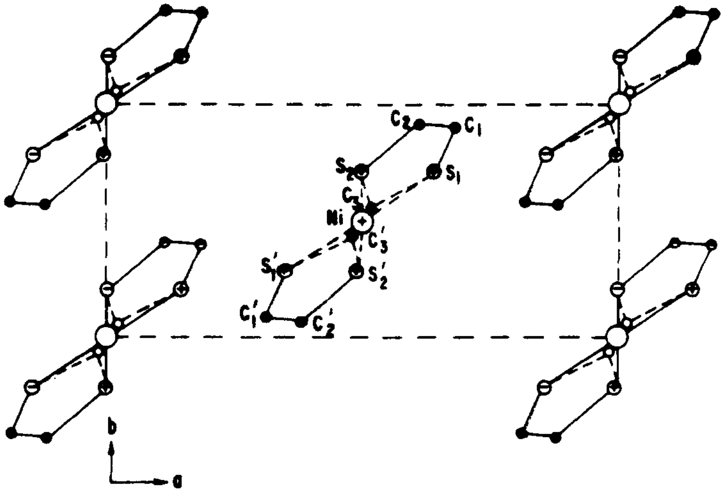


FIGURE 1 Projection of the crystal structure of $(TTF)_2[NiS_4C_4H_4]_3$ on the (001) plane (from Ref. 17).

ecule appears as expected for the individual TTF and $NiS_4C_4H_4$ species. A detailed analysis of the satellite reflections revealed that the structure is compositionally modulated. Thus, the site occupancy factors for the two types of molecules varies sinusoidally along the x and y directions of the monoclinic cell to form a superstructure whose a' and b' cell parameters are related to those of the average structure by the relations $a' = 2a$ (subcell) and $b' = 5b$ (subcell).

In contrast to the neutral molecular nature of the TTF and $NiS_4C_4H_4$ units in $(TTF)_2[NiS_4C_4H_4]_3$, in the case of the corresponding $(TTF)_2[NiS_4C_4H_4]$ derivative we find that charge transfer has occurred to give TTF^+ and $NiS_4C_4H_4^-$ species which crystallize along with a neutral TTF molecule to form another novel structure in which the TTF^+ units are arranged in one-dimensional stacks of alternating $(TTF^+)_2$ dimers and TTF^0 species.[16]

On the basis of these observations it is apparent that this particular combination of donor and acceptor molecules must be close to the cross-over point for electron transfer in the solid state, such that differences in stoichiometry and structure of the type observed are sufficient to cause a switch from essentially zero to complete charge transfer.

The implication that the occurrence of solid state charge transfer is a critical factor in determining the structures and properties of π-donor–acceptor compounds and that the redox potentials for these donors and acceptors might be useful in assessing the degree of solid state charge transfer has been well recognized in this area.[18] If the aim is to obtain a segregated, two-stack structure analogous to that in TTF-TCNQ, it is apparent that these redox potentials should be closely matched to promote partial charge transfer in the solid state. Analysis of a wide range of π-DA compounds indicates that the following empirical relationship between the redox potentials of the donor and acceptor may have to be satisfied, along with other factors such as the overall planarity and electronic structure of the molecular units, in order to obtain "TTF-TCNQ"-like solids: $E_D^{0\,+} - E_A^0 = 0.1\text{–}0.4$ V.[18]

Replacement of the H atoms in the $MS_4C_4H_4$ complexes by CF_3 groups results in a substantial increase in the oxidizing strength of the neutral complexes such that complete electron transfer with π-donors such as TTF occurs on mixing in solution (i.e., $E_D^{0\,+} - E_A^0 < 0$ V). The compounds obtained from such reactions involving the neutral $MS_4C_4(CF_3)_4$ (M = Ni and Pt) complexes and TTF in acetonitrile solution are sparingly soluble, 1:1 π-DA compounds whose formulation as ionic, $(TTF^+)[MS_4C_4(CF_3)_4^-]$ salts is supported by both magnetic properties and crystal structure determinations.[19] The same compounds were also obtained by means of metathesis reactions, involving $(TTF)_xCl$ and alkylammonium $[MS_4C_4(CF_3)_4]^-$ salts. This latter approach also permitted preparation of the corresponding M = Cu and Au derivatives, which are not available in the form of the neutral $MS_4C_4(CF_3)_4$ complexes.

In this manner five different $(TTF)[MS_4C_4(CF_3)_4]$ compounds were obtained whose crystal structures show a remarkable degree of similarity.[19] In fact, all but one of these compounds (with M = Ni) are isostructural, crystallizing in a triclinic structure in which the two types of ions alternate along the three nearly orthogonal directions to form a NaCl-like lattice (Fig. 2). Due to the planar nature of these ions, there is a stacking of alternate D^+ and A^- units along one direction (*c*). However, the separation between the units is large (ca. 3.9 Å) and the different symmetry of the respective HOMOs leads to little direct electronic interaction between the ions. Thus, these compounds are all good electrical insulators and, at room temperature, their magnetic moments are consistent with the presence of discrete TTF^+ and $[MS_4C_4(CF_3)_4]^-$ ions. The TTF^+ cations contain one unpaired spin per formula unit. However, the MBDT complexes in this case can have either one (M = Pt) or no (M = Cu and Au) unpaired electrons.

Depending on the nature of the metal ion, these compounds exhibit a wide range of novel magnetic phenomena ranging from bulk ferrimagnetism in the case of the Ni compound to spin-Peierls transitions for the Cu and Au derivatives (Fig. 3).[20] Among the isostructural $(TTF)[MS_4C_4(CF_3)_4]$ compounds, the M = Pt derivative alone has unpaired electrons on both donor and acceptor units. The description which appears appropriate to this compound is that of a system of 1-D ferromagnetic chains which couple antiferromagnetically with one another at low temperature.

Replacement of the Pt by the Cu or Au has little effect on the structure. However, the diamagnetic character of the respective $[MS_4C_4(CF_3)_4]^-$ ions leads to an entirely different situation insofar as the magnetic properties are concerned. In this case direct mag-

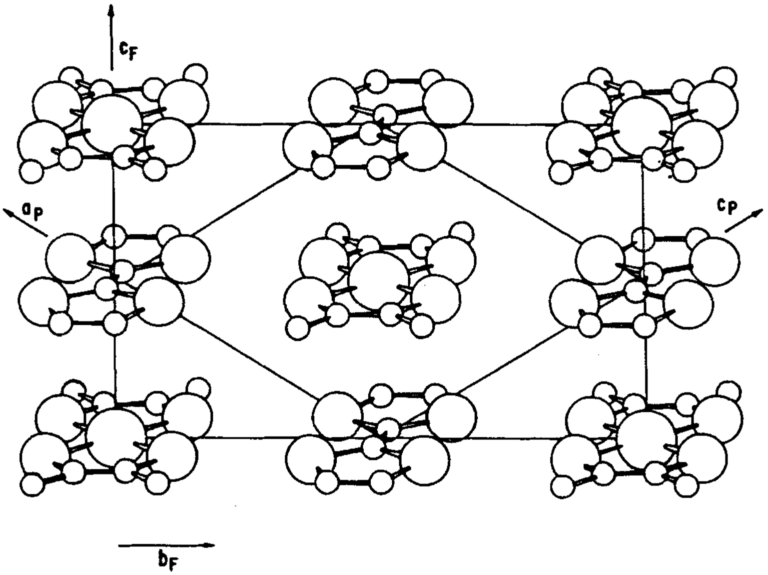


FIGURE 2 Arrangement of TTF and $MS_4C_4(CF_3)_4$ units in the (100) plane of the F$\bar{1}$ cell and (010) plane of the P$\bar{1}$ cell of the (TTF)[$MS_4C_4(CF_3)_4$] complexes (M = Pt, Cu, Au). The largest circle represents the metal M at the center of the $MS_4C_4(CF_3)_4$ unit. The F atoms of the CF_3 groups and the H atoms of TTF have been omitted for clarity of representation (from Ref. 19).

netic interactions along the molecular stacking direction is precluded by the presence of the diamagnetic $[MS_4C_4(CF_3)_4]^-$ (M = Cu and Au) ions. However, owing to a subtle structural change which occurs just below room temperature in these compounds, magnetic interactions are possible along a diagonal direction to the stacking axis involving direct exchange among the TTF^+ ions (Fig. 2).[21] This first-order structural transition destroys the essential equality of the a_P and c_P dimensions at room temperature and reduces the TTF^+ unit separation along c_P. As is suggested by the results of the magnetic property measurements, this is sufficient to induce a quasi-1-D AF exchange interaction along c_P, resulting in a c vs. T dependence which can be accurately fit by a Bonner–Fisher calculation of a $S = 1/2$, 1-D uniform Heisenberg AF chain. Below 12 K for M = Cu and 2 K for M = Au, the spin susceptibility decreases sharply, independent of the orientation of the crystals in the applied field, and falls to zero within a few degrees.[22]

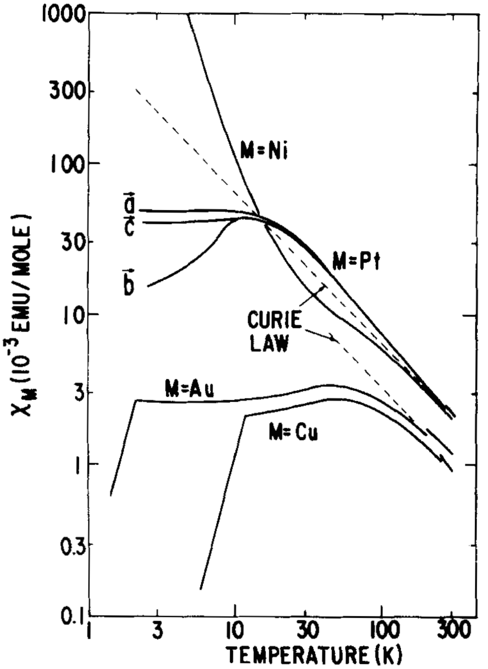


FIGURE 3 Magnetic susceptibility vs. temperature for the (TTF)[$MS_4C_4(CF_3)_4$] complexes (M = Pt, Cu, Au) (from Ref. 20).

The temperature dependence in this region was found to conform in good qualitative detail to that expected for a system undergoing the progressive, temperature-dependent dimerization of spins anticipated for the spin-Peierls transition.[22] The potential existence of such a transition had been theoretically predicted almost two decades prior to its first observation in these systems and it acquired the name "spin-Peierls transition" by virtue of its close analogy to the Peierls transition in the 1-D metal systems. In the spin-Peierls case the transition is second order and is driven by the spin subsystem. Below T_c(SP) the system is dimerized, forming a singlet ground state with a magnetic gap.

Subsequent to the first report of this transition in the (TTF)[$MS_4C_4(CF_3)_4$] (M = Cu, Au) system in 1976,[22] a large number of papers have appeared on this subject[23–26] reporting the results of both theoretical and experimental investigations on these and the two other well characterized members of this apparently very limited class of materials, MEM$(TCNQ)_2$ (T_c = 18 K)[24] and the selenium analog of the TTF(CuBDT) complex, (TTF)-$[CuSe_4C_4(CF_3)_4]$ (T_c = 6 K).[25] As a result of these studies much has been learned about the nature of this transition and its dependence on such parameters as magnetic field, pressure and chemical substitution. The availability, in particular, of a homologous series of compounds with the same structure, i.e., the (TTF)$[MY_4C_4(CF_3)_4]$ (Y = S, M = Cu, Au and Y = Se, M = Cu) derivatives, has provided a range of transition temperatures within a common structural framework enabling the systematic study of the effects of subtle structural changes on T_c(SP).[26]

THE M$(dmit)_2$ COMPLEXES

In addition to TTF, various other organic π-donors[10c,14,27,28] as well as certain macrocyclic metal complexes[10c,14,29,30] have been employed in reactions with simple ethylenedithiolene metal complexes both in our laboratories and elsewhere. It is noteworthy that among all these bisdithiolene metal complex-containing π D-A compounds, metal-like properties have been evidenced only in compounds where the organic donor (for example, perylene[14] or TTT[27]) is primarily responsible for the high conductivity. Thus, prior to 1981 the partially oxidized $(H_3O)_{0.33}Li_{0.82}[PtS_4C_4(CN)_4]$ complex[15] constituted the only example of a highly conductive bisdithiolene metal complex system in which the conduction occurred through interacting MBDT units. This situation changed dramatically with the application of a new class of bisdithiolene metal complexes employing the dmit ligand ($dmit^{2-}$ = 1,3-dithiol-2-thione-4,5-dithiolate) (**2**).

At about this time in the development of the field of molecular conductors and superconductors, following the observation of superconductivity in the absence of applied pressure in the case of $(TMTSF)_2ClO_4$,[31] synthetic work in the area began to focus increasingly on the development of systems with enhanced interstack interactions. The observation of ambient-pressure superconductivity for certain members of the series of $(BEDT\text{-}TTF)_2X$ compounds, which also exhibit interstack (sulfur . . . sulfur) interactions,[32,33] seemed to confirm the hypothesis that increasing the dimensionality (1-D to 2- or 3-D) of the system could obviate the ubiquitous metal-to-insulator transition encountered on cooling most previously studied 1-D metals to low temperatures, arising from the Peierls instability[7] associated with a true 1-D metallic system.

In both the $(TMTSF)_2X$ and $(BEDT\text{-}TTF)_2X$ compounds relatively short interstack interactions were observed involving selenium or sulfur atoms on the periphery of the molecules. A simple strategy[34] for enhancing interstack interactions followed. This involved the incorporation of additional sulfur or selenium atoms on the periphery of molecular candidate systems which were effectively coupled into the π-electronic system of the molecule. Whereas TMTSF contains four selenium atoms and BEDT-TTF eight sulfur atoms on their periphery, the transition metal complexes derived from the dmit ligand, $[M(dmit)_2]^{n-}$ (**2**), have ten peripheral sulfur atoms at their disposal to establish interstack interactions. Like the parent ethylenedithiolene ligands, dmit can be used for the preparation of various transition metal complexes $C_n[M(dmit)_2]$, with different metals (M = Zn, Ni, Pd, Pt, Cu, Au, Fe . . .), counter-cations ($C = Na^+$, R_4N^+, Ph_4As^+ . . .) and formal oxidation states ($n = 2, 1, 0$).[35-42] Unlike the bis-ethylenedithiolene complexes, these complexes readily undergo partial oxidation to give the anion-radical salts $C_x[M(dmit)_2]$.[36-38,40,42]

Most of the $C_x[M(dmit)_2]$ compounds were grown on a platinum electrode by electrochemical oxidation of the monovalent salt.[43] The results of an extensive series of structural studies on these $C_x[M(dmit)_2]$ compounds indicate that the strategy for enhancing interstack interaction by increasing the number of sulfur atoms on the periphery of the molecule actually was successful. In fact all of these compounds exhibit an extended network of relatively short sulfur . . . sulfur contacts.[38,40,42] These short sulfur . . . sulfur contacts occur not only within the stacks but also between molecules of adjacent stacks. This structural two-dimensionality is reflected in the low anisotropy of the conductivities.[36c,38]

As is quite common for molecular metals, several phases with different, or even the same, stoichiometries have been identified for several of the $C_x[M(dmit)_2]$ compounds.[44,45] In the case of $(n\text{-}Bu_4N)_x[Pd(dmit)_2]$, for example, two main phases with stoichiometry $x = 0.33$ and $x = 0.5$ were isolated in the course of electrochemical preparation. Their overall structures are only slightly different and are both characterised by the stacking of $[Pd(dmit)_2]_2$ dimers. Nevertheless, their conductivity behaviors are markedly different.[44]

The different mixed valence salts $C_x[M(dmit)_2]$ exhibit various conductivity behaviors. Some are high temperature metals but most are insulators or semiconductors. Until recently, none of the $C_x[M(dmit)_2]$ compounds exhibited metal-like behavior down to low temperatures or superconductivity. The $(Me_4N)_{0.5}[Ni(dmit)_2]$ compound described by Kobayashi and co-workers[40b,c] does undergo a superconducting transition at 5 K under an applied pressure of 7 kbar.

These results show clearly that the $M(dmit)_2$ complexes can form a conductive network in a molecular solid in the absence of organic molecules with extended π-electronic systems such as TTF. On the other hand, the $M(dmit)_2$ complexes may also be used as acceptors for the preparation of conductive π donor–acceptor compounds with TTF-like donor molecules. A number of these compounds, $D[M(dmit)_2]_y$, with various donors (D = TTF, TMTTF, TTMTTF, DBTTF, TMTSF, EDT-TTF, TSF, HMTTeF, . . .), metals (M = Ni, Pd, Pt, Au) and stoichiometries ($y = 1, 2, 3$) have been obtained.[46–50]

As is the case for the $C_x[M(dmit)_2]$ salts, these $D[M(dmit)_2]_y$ compounds exhibit a wide range of novel structures and physical properties. The $TTF[Pd(dmit)_2]_2$ system affords a clear example of the potential for novel and highly complex structure/property relationships afforded by the dmit complexes. This compound is obtained in at least three crystalline phases (α, α′, δ) with different electrical and structural properties.[51] Although none of these different phases remain metallic at low temperature, the α′ and α phases were found to undergo a complete superconducting transition under pressure, 5.93 K at 24 kbar and 1.7 K at 22 kbar, respectively.[52] Analysis of the temperature–pressure phase diagram of α′-$TTF[Pd(dmit)_2]_2$ shows that, contrary to the organic superconductors such as $(TMTSF)_2PF_6$,[53] no Spin Density Wave (SDW) ground states are observed in the vicinity of the superconducting state.[52] At low pressures and between 70 and 250 K, a gradual localization of the carriers leads to a small gap semiconductor or a semimetal. In fact, ambient pressure X-ray diffuse scattering experiments provide evidence of Charge Density Wave (CDW) instabilities which compete with superconductivity under pressure.[54]

Unlike all of the metal-like TTF[Pd(dmit)$_2$]$_2$ phases which undergo, at ambient pressures, a metal-to-insulator transition, the analogous nickel compound, TTF[Ni(dmit)$_2$]$_2$, exhibits a metal-like conductivity behavior down to 2 K,[46] is not superconducting above 47 mK, but undergoes a complete superconducting transition (1.62 K at 7 kbar).[55] Moreover, TTF[Ni(dmit)$_2$]$_2$ is the first molecular superconductor in which the transition temperature increases with increasing pressure.[56] As shown in the phase diagram (Fig. 4), at high pressures, superconduction coexists (and does not compete as in the case of α'-TTF[Pd(dmit)$_2$]$_2$) with a high-pressure condensation mode of the carriers.[57] At lower pressure, the superconducting state stumbles upon a low pressure insulating ground state and is re-entrant at very low temperature, in a narrow pressure range around 5.3 kbar.

The structure of TTF[Ni(dmit)$_2$]$_2$, as well as those of the isostructural α- and α'-TTF[Pd(dmit)$_2$]$_2$ compounds, can be described as consisting of segregated stacks of the donor TTF and the acceptor M(dmit)$_2$ molecules (Fig. 5).[46,51] Moreover, a number of short interstack S . . . S contacts are observed between M(dmit)$_2$ units in adjacent stacks, and between M(dmit)$_2$ units and TTF molecules. Therefore, from a structural perspective, TTF-[Ni(dmit)$_2$]$_2$, and α- and α'-TTF[Pd(dmit)$_2$]$_2$, appear to be 2-D, or even 3-D. In fact, a low anisotropy in the magnetoresistance of TTF[Ni(dmit)$_2$]$_2$ is observed,[58] but ^{1}H NMR measurements indicate that the TTF stacks are 1-D.[59] This 1-D character seemed to be confirmed at first by LUMO-based band structure calculations.[60] However, more elaborate calculations, including HOMO bands in addition to the LUMO bands, suggest the existence of a 2-D hole pocket in the Brillouin zone of TTF[Ni(dmit)$_2$]$_2$, whereas α'-TTF[Pd(dmit)$_2$]$_2$ remains more 1-D.[61]

These calculations help to rationalize the results obtained by the magnetoresistance,[58] X-ray diffuse scattering,[54,62] ^{1}H and ^{13}C NMR studies[59,63] and the differences in the phase diagrams of these two compounds,[57] as well as the behavior of dimerized systems such as (Me$_4$N)$_{0.5}$[Ni(dmit)$_2$] and δ-TTF[Pd(dmit)$_2$]$_2$.[61] In particular, the

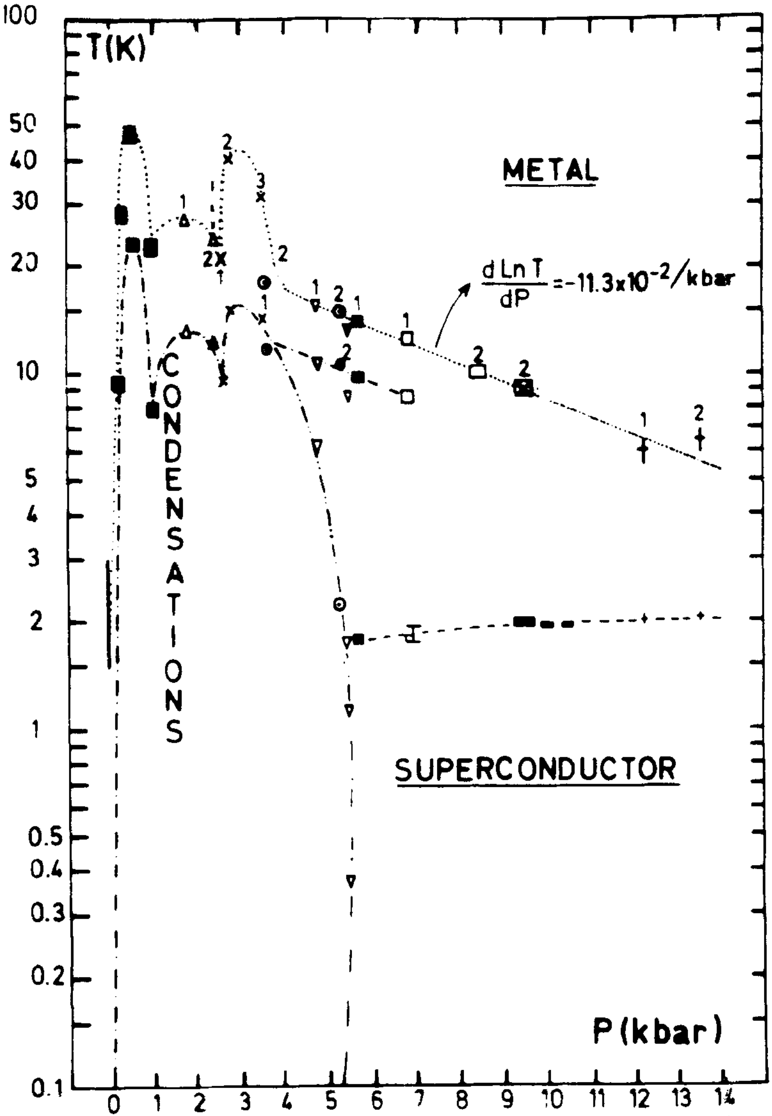


FIGURE 4 Phase diagram (T, P) of TTF[Ni(dmit)$_2$]$_2$. The curves (· · ·) and (- · - · - · -) show the pressure dependence of the temperatures of the resistivity minimum and of the inflexion point of the Log(resistivity) vs. 1/*T* curve, respectively. The curve (- - -) shows the pressure dependence of the superconductive critical temperature. The curve (- · · - · · -) shows the phase separation between the superconductive ground state and the low pressure CDW insulating state (from Ref. 57).

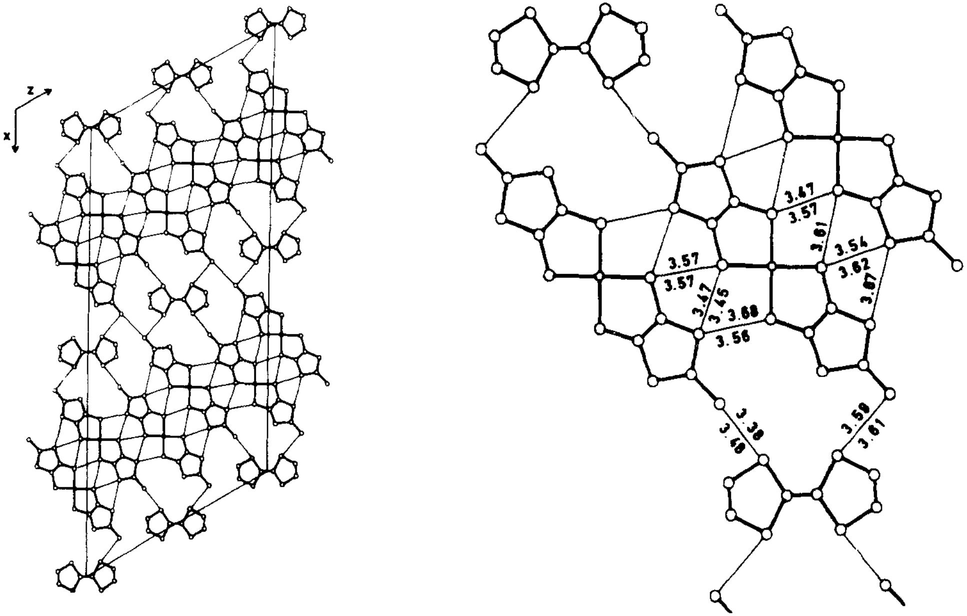


FIGURE 5 (Left) Projection of the crystal structure of TTF[Ni(dmit)$_2$]$_2$ on the (010) plane. Thin lines indicate S . . . S distances shorter than 3.70 Å. (Right) Blow-up of a portion of this projection. Crystallographically independent S . . . S distances (Å) are indicated (from Ref. 46).

pressure dependence of the resistivity minimum associated with the low-pressure condensation mode of TTF[Ni(dmit)$_2$]$_2$ may result from Pressure Induced Charge Density Waves. In fact, ambient pressure X-ray diffuse scattering experiments also provide evidence for CDW instabilities in TTF[Ni(dmit)$_2$]$_2$.[54,62]

The results obtained thus far have shown that small changes in the chemistry of the M(dmit)$_2$ systems may lead to new compounds exhibiting novel physical properties. From the chemical perspective, other studies on M(dmit)$_2$ systems have been carried out or are underway, including chemical modifications of the dmit ligand by substituting sulfur for oxygen[64] or selenium[65]; extension of the dmit ring system by incorporating additional peripheral sulfur atoms[66]; variation in the nature of the donor molecule or the countercation,[67] etc.

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3. Abbreviations: TCNQ, tetracyanoquinodimethane. TTF, tetrathiafulvalene. TMTSF, tetraselenafulvalene. MBDT, bis-dithiolene metal complexes. MEM, methylethylmorpholinium. dmit, 1,3-dithia-2-thione-4,5-dithiolato. TTT, tetrathiotetracene. BEDT-TTF, bis-ethylenedithiatetrathiafulvalene. TSF, tetraselenafulvalene. TMTTF, tetramethyltetrathiafulvalene. TTMTTF, tetrathiomethyltetrathiafulvalene. DBTTF, dibenzotetrathiafulvalene. HMTTeF, hexamethylenetetratelurafulvalene. EDT-TTF, ethylenedithio-tetrathiafulvalene.

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