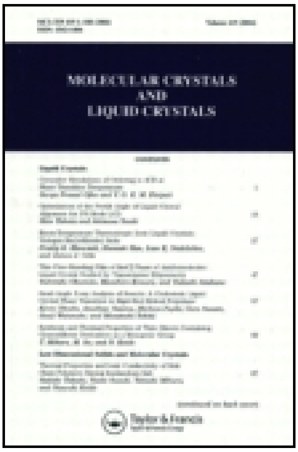

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Design of Organic Superconductors: Successes and Disappointments

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DESIGN OF ORGANIC SUPERCONDUCTORS: SUCCESSES AND DISAPPOINTMENTS

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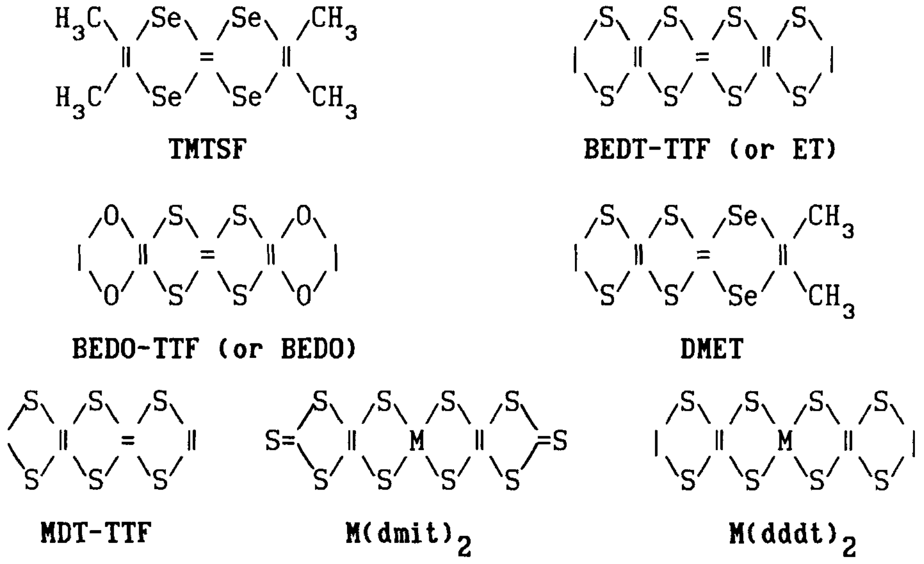
Abstract Some structural and chemical approaches applied to the construction of organic superconductors are discussed. A retrospective view from the first quasi one-dimensional superconductors (TMTSF salts) to quasi two-dimensional BEDT-TTF salts and recent three-dimensional fullerene complexes is presented.

INTRODUCTION

Superconductivity in organic compounds was discovered in 1980. Of about forty organic superconductors had been found since, their T_c enhancing gradually from 1 to 30 K. In their chemical nature, all these compounds are either cation radical salts based on TTF-derivatives (TMTSF, ET, BEDO, DMET, MDT-TTF) or anion radical salts based on the $M(dmit)_2$ complexes and fullerene (C_{60}) complexes (Fig.1).
'Organic superconductivity' was first found under pressure in the cation radical salt $(TMTSF)_2PF_6$.[1] On one hand, it was a lucky finding, on the other, it became a logical accomplishment of a 10-year search for organic superconductors. By that time, stable organic metals, halogenides of tetraselenotetracene, with conductivity higher than 10^5 at helium temperature had been found.[2] Though these first really stable organic metals appeared to be nonsuperconducting, the fact of a stable metallic state existence in organic compounds itself indicated that organic superconductivity was possible.
In 70s, quasi one-dimensional conductors based on ion

radical salts, which contained two conducting systems of opposite signs, a cation radical system (mainly TTF and its derivatives) and an anion radical one (TCNQ), were the main objects of the research. By the end of 70s, this direction had been exhausted with no superconductivity found. It became evident that salts containing one cation radical system only could be the base for stable organic metals.



TMTSF **BEDT-TTF (or ET)**

BEDO-TTF (or BEDO) **DMET**

MDT-TTF **$M(dmit)_2$** **$M(dddt)_2$**

FIGURE 1 Donor and acceptor molecules, used as the base of organic superconductors (except $M(dddt)_2$)

TMTSF SALTS

The first TMTSF cation radical salts (including $(TMTSF)_2PF_6$) were synthesized by Bechgaard *et al.*[3] The choice of Se-containing donors was determined by the fact that on the introduction of larger selenium atoms (as compared with those of sulfur) into the donor molecule, shortened Se...Se contacts might appear not only inside the cation stacks, but in the transverse direction as well, which contributed much to the enlarging of the electron system dimension. By the beginning of 80s, it had become evident that quasi one-dimensional conductors were not perspective in the superconductivity search because of their considerable dielectric instabilities at low temperatures.

TABLE I Molecular organic superconductors based on TMTSF cation radical salts

No.	Salt	T_c, K	P, Kbar	Ref.
1	$(TMTSF)_2PF_6$	0.9	12.0	1
2	$(TMTSF)_2AsF_6$	0.9	12.0	4
3	$(TMTSF)_2SbF_6$	0.4	11.0	4
4	$(TMTSF)_2TaF_6$	1.4	12.0	4
5	$(TMTSF)_2FSO_3$	2.0	6.5	5
6	$(TMTSF)_2ReO_4$	1.3	9.5	4
7	$(TMTSF)_2ClO_4$	1.2	0	4

The discovery of superconductivity in $(TMTSF)_2PF_6$ stimulated the synthesis of other TMTSF salts with octa- and tetrahedral anions. This led to the finding of six more superconductors including that at ambient pressure, $(TMTSF)_2ClO_4$ (Table I). However, soon it became clear that the range of TMTSF-based superconductors was rather limited in the synthetic aspect. They all had only one superconducting structure and low values of T_c (Table I). The superconducting structural motif was determined by the donor molecule packing. Methyl groups from the neighboring TMTSF stacks formed cavities for anions of certain size and geometry only (Fig.2). The attempts to considerably extend the number of superconductors based on TMTSF appeared to be a failure.

The TMTSF salts are similar to quasi one-dimensional conductors in their electronic structure and properties. At ambient pressures they show metal-dielectric transitions caused by the spin density waves or by ordering of the anions.[6]

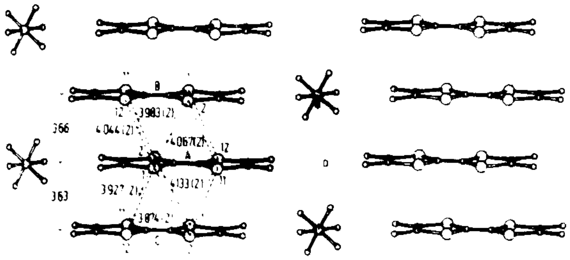


FIGURE 2 $(TMTSF)_2PF_6$. A side view of TMTSF stacks (tilted at 10°) showing shorter Se•••Se distances (Å) within a stack[7].

ET SALTS

Another important achievement in the design of organic superconductors is concerned with the synthesis of quasi two-dimensional metals based on cation radical ET salts, which are less sensitive to dielectric instabilities. A ET molecule contains eight sulfur atoms and saturated noncoplanar CH_2CH_2 groups. The former promote the formation of multiple side-by-side S...S contacts in the cation radical layers[8] (Fig.3) and the latter create some steric hindrances for the intrastack S...S contacts that is conducive to equalization of interactions inside the conducting layers. It should be noted that for a long time the condition of strict planarity of the donors and acceptors was considered as one of the most important structural requirements to the components of the conducting ion radical salts. However, it provoked strong one-dimensional interactions in them and consequently dielectrization of the electronic system at low temperatures.

The anisotropy of conductivity in the ET layers is either small or is not observed at all. At the same time, it is large in the direction perpendicular to the layer plane (within 400-10^4 for different salts).[9] Cation and anion layers alternate along this direction (the *c* axis, Figs.3,4).

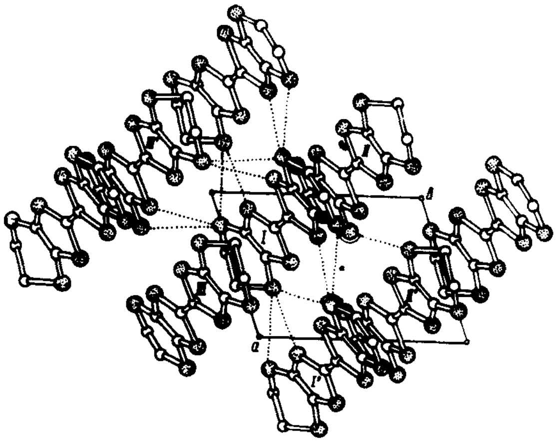


FIGURE 3 β-$(ET)_2I_3$. The ET layer projection along the *c* direction.[8] Shortened interstack contacts for each independent ET cation (I) are shown with dashed lines.

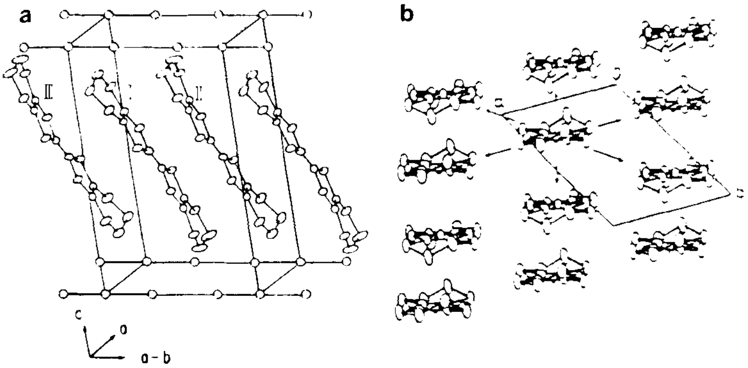
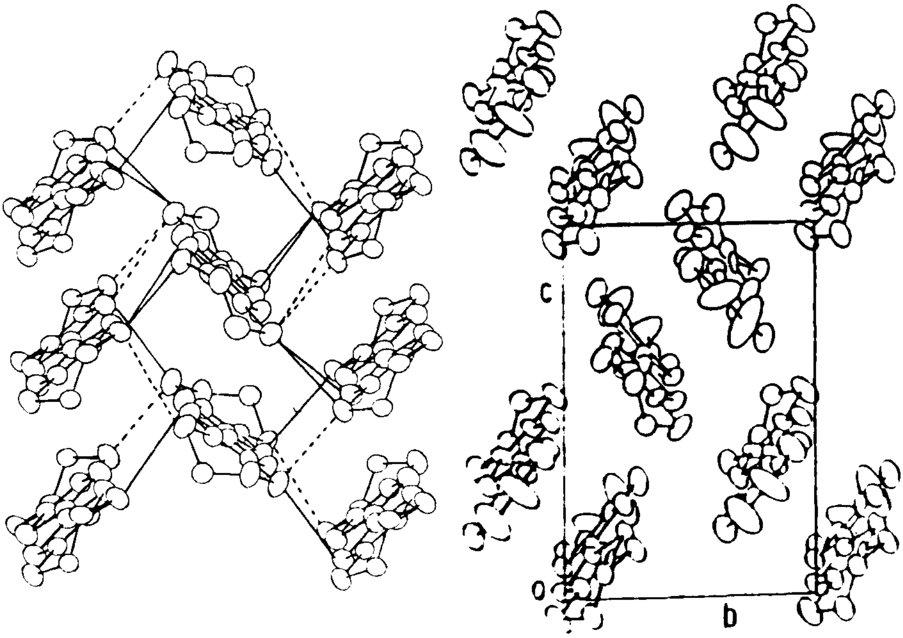


FIGURE 4 β-$(ET)_2I_3$. Arrangement of the ET cations within a column (*a*) and their packing within each donor layer (*b*)[10].

Superconductors of the ET family may be divided into three groups according to the mode of the internal structure of their cation layer, those of β-, α-, and κ-types. In β-superconductors the ET layers are composed of parallel ET stacks (Fig.4*b*), in α-ones stacks are not parallel[11,12] (the angle between the cation planes of neighboring stacks comprises ~80°, Fig.5*a*); there are no stacks in the κ-type layers, they are composed of the ET pairs situated almost perpendicular to each other in a parquet-like manner (Fig.5*b*)[13]. The α-structure is not a common case among superconductors of the ET family. Though a number of the α-type ET salts have been synthesized so far, two of them only, α-$(ET)_2[(NH_4)Hg(SCN)_4]$[14] and θ-$(ET)_2I_3$)[15], undergo superconducting transitions. The β-and κ-structures are



a b

FIGURE 5 Packing of ET cations within donor layers of α-$(ET)_2[(NH_4)Hg(SCN)_4]$ (*a*)[11] and κ-$(ET)_2Cu(NCS)_2$ (*b*)[13].

characteristic of the majority of the ET-based superconductors.

The first ET salts were synthesized with tetrahedral anions ClO_4[16] and ReO_4[17] in 1982-83. The ReO_4-containing

TABLE II Molecular organic superconductors based on ET and its symmetric derivative BEDO-TTF

No.	Salt	T_c, K	P, Kbar	Ref.
1	β_L-$(ET)_2I_3$	1.5	0	18
2	β_H-$(ET)_2I_3$	7-8	0; 0.5	19-25
3	β-$(ET)_2IBr_2$	2.0-2.8	0	26,27
4	β-$(ET)_2AuI_2$	4.5	0	28
5	α-$(ET)_2[(NH_4)Hg(SCN)_4]$	1.1	0	14
6	θ-$(ET)_2I_3$	3.6	0	15
7	κ-$(ET)_2I_3$	3.6	0	29
8	κ-$(ET)_2Cu(NSC)_2$	10.4	0	30
9	κ-$(ET)_2Cu[N(CN)_2]Br$	11.6	0	31
10	κ-$(ET)_2Ag(CN)_2H_2O$	5.0	0	32
11	κ-$(ET)_4Hg_{2.89}Br_8$	4.3	0	33,34
		6.7	3.5	35,36
12	$(ET)_2Hg_{1.41}Br_4$	2.0	0	37
13	γ-$(ET)_3(I_3)_{2.5}$	2.5	0	38
14	κ-$(ET)_2Cu[N(CN)_2]CN$	11.2	0	39
15	κ-$(ET)_4Hg_{3-\delta}Cl_8$	1.8	12	40
		5.3	29	41
16	κ-$(ET)_2Cu[N(CN)_2]Cl$	12.5	0.3	42
17	$(ET)_2ReO_4$	2.0	4.5	17
18	$(ET)_3Cl_2 \cdot 2H_2O$	2.0	16.0	43
19	κ-$(ET)_2Cu_2(CN)_3$	2.8	1.5	44
		3.8	0	39
20	κ-$(ET)_4Pt(CN)_4 \cdot H_2O$	2.0	6.5	45
21	β_m-$(BEDO\text{-}TTF)_3Cu_2(NSC)_3$	1.0	0	46
22	$(BEDO\text{-}TTF)_2ReO_4 \cdot H_2O$	2.0	0	47,48

salt appeared to be a superconductor under the presure of 4.5 kbar ($T_c \simeq 2$ K). However, the attempts of increasing the number of ET-based superconductors with tetra- and octahedral anions, which worked so well in the case of Bechgaard salts, appeared to be unsuccessful.

In 1984 the first sulfurorganic superconductor with $T_c \simeq$ 1.5 K at ambient pressure was synthesized.[18] It was an ET salt with the linear anion I_3, β-$(ET)_2I_3$. Soon after, it was found that the compound could exist in low- (β_L) and high-temperature (β_H) superconducting states with $T_c \simeq 1.5$ and $\simeq 8$ K, respectively.[19] The further progress in the search for organic superconductors was much affected by these results. The quest developed in two directions, variations of the anions in the ET salts and chemical modification of the cation radical system itself. Both approaches appeared to be rather fruitful and led to the increase of the number of organic superconductors up to ~40 and to the enhancement of their critical temperature up to 12.5 K (Table II). The ET salts along with the recently obtained fullerene complexes remain the main objects in the search for new superconductors.

Variations of Anions in ET Salts

Since the discovery of superconductivity in β-$(ET)_2I_3$, variations of the anions in ET-salts were concerned at first mainly with the substitution of I_3 for some other linear anions, such as mixed polyhalide anions IBr_2, I_2Br, ICl_2 *etc.* and metal complex anions of the MX_2-type (M is Cu, Ag, Au; X is a halogen).[49,50] It should be noted that all these anions are somewhat shorter than I_3 (10.1 Å). It was found that superconducting salts with the β_H-$(ET)_2I_3$ structure were formed only in the case of anions, which were very close in their size to I_3 (*e.g.*, AuI_2 9.4 Å and IBr_2 9.3 Å). The absence of superconductivity in the β-salt with the I_2Br anion (the closest to I_3) is likely to be caused by the disorder, which arises in the lattice of this salt because of the I_2Br anion asymmetry.[49] In contrast to traditional inorganic superconductors, structural disorder affects much the T_c of organic low-dimensional superconductors. The β_L modification of $(ET)_2I_3$ differs from the β_H one in the presence of an incommensurate lattice modulation [51-54] giving rise to an additional source of electron scattering, so that its residual resistance is some 20 times higher than in the completely ordered β_H-modification (Fig.6).[25] The T_c of the latter is 5 times higher than that of the β_L-modification.

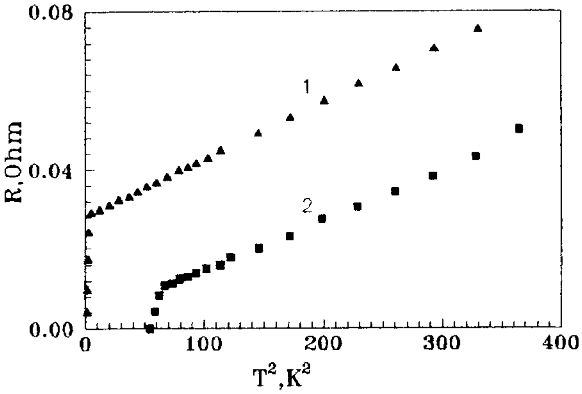


FIGURE 6 Temperature dependence of the resistivity of β_L-$(ET)_2I_3$ (1) and β_H-$(ET)_2I_3$ (2) phases at low temperatures.[25]

An observation that T_c increases within the group of isostructural completely ordered β-salts ($(ET)_2X$, X=IBr_2, AuI_2, I_3; Table II) with the size of the linear anion[55] became a clue to the search for salts with higher T_c, which led to the synthesis of $(ET)_2Cu(NCS)_2$ with T_c = 10.4 K.[30] However, this salt was found to have a different ET layer packing (κ-type) with parquet-like arrangement of ET cations within a sheet (Fig.5*b*) and anion layers consisting of zig-zag polymer chains instead of discrete linear anions. This result stimulated the search for other polymer metal complex anions as counterions and led to the synthesis of κ-$(ET)_2Cu[N(CN)_2]Br$[31] and κ-$(ET)_2[CuN(CN)_2]Cl$[42] with $T_c \simeq 11.5$ and 12.5 K respectively, which are the highest values attained for ET salts (Fig.7). The latter salt is a semiconductor under normal conditions, its superconductivity being manifested at slightly elevated pressure (0.15-0.3 kbar)[42,56] or at 'ambient pressure' under a stress effect.[57,58] At present the synthesis of new ET salts with polymer metal complex anions seems to be the most promising direction in the search for superconductors with higher T_c.

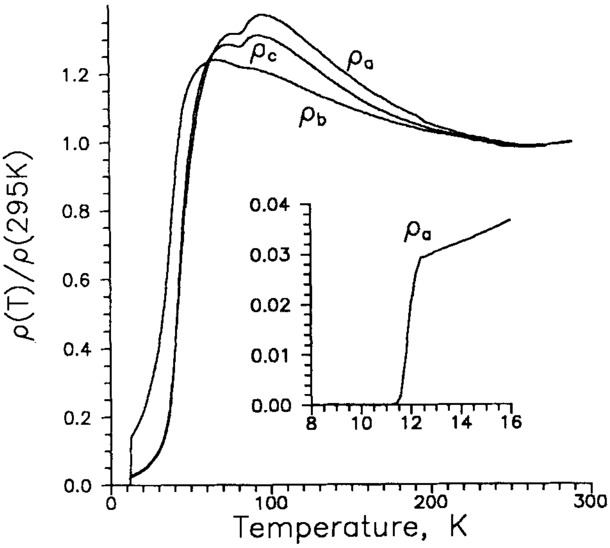


FIGURE 7 κ-$(ET)_2Cu[N(CN)_2]Br$. The temperature dependence of the normalized resistivity in the *a*, *b*, and *c* directions.[59] The ρ_b/ρ_a and ρ_b/ρ_c values are of about 10^3 at ambient temperature. The insert shows the superconducting transition.

Out of twenty ET-based superconductors known so far, ten contain polymer metal complex anions (Table II).

Chemical Modifications of the ET Molecule

Chemical modification of the ET molecule is developing in three directions:

(*i*) variations of the terminal bridge groups;

(*ii*) replacement of heteroatoms (sulfur for selenium or oxygen) and the central C=C bond by a metal;

(*iii*) synthesis of asymmetric ET derivatives.

The replacement of peripheral ethylene groups of ET by those of propylene, methylene, vinylene *etc.* did not give rise to the synthesis of new organic superconductors.[50,60] The $(PT)_2I_3$ and $(PT)_2IBr_2$ salts though being isostructural to β-$(ET)_2I_3$ appeared to be semiconductors.[61-63] Contrary to β-$(ET)_2I_3$, β-$(PT)_2I_3$ has short intercation contacts along the stacks and noticeable anisotropy of conductivity is observed in the plane of the PT layer. The analysis of intermolecular interactions in β-$(PT)_2I_3$ showed that electronic structure of the salt was quasi one-dimensional.[64] *A priori* the substitution of the ethylene bridge for a more bulky propylene one did not seem to affect the interaction in the PT stacks. However, their flexibility allows the cations to be packed more tightly than in β-$(ET)_2I_3$.

Considerable hopes have been associated with substitution of sulfur atoms in the ET molecule for selenium ones. In particular, sulfur substitution for selenium in quasi one-dimensional conductors results in stabilization of the metallic state owing to some increase in the dimension of the electronic system.

All possible symmetric selenium analogs of ET have been synthesized: completely substituted BEDSe-TSeF and partially substituted BEDSe-TTF and BEDT-TSeF. Cation radical salts of these donors with various anions have been synthesized.[65-68] Some of them based on BEDT-TSeF are stable metals up to 4 K, however, superconducting transitions have not been observed in any of them. The

BESeT-TTF salt with the I_3 anion is isostructural to β-$(ET)_2I_3$, however, it becomes an insulator at low temperature.[67] Electroconducting properties of the ET salts and their derivatives are determined by a fine balance of intralayer cation radical interactions resulting in quasi one- or two-dimensional electronic structures. This balance in its turn is determined by the mode of the cation radical overlapping, the number and length of chalcogene-chalcogene contacts in different directions in the layer. Minor changes in the values of these parameters affect much conducting properties.

Along with the S replacement by heavier Se, a work has been produced on introduction of lighter oxygen atoms into ET. One of such ET analogs, BEDO-TTF, has been obtained.[69] A number of BEDO-TTF salts were found to be metals,[46-48,69,70] two of them only being superconductors with $T_c \approx 1$-2 K (Table II).

The discovery of superconductivity in TMTSF and ET salts has stimulated the synthesis a hybrid noncentrosymmetric DMET molecule, which consists of one half of TMTSF and of one half of ET (Fig.1). Seven superconductors have been

TABLE III Molecular organic superconductors based on ET asymmetric derivatives

No.	Salt	T_c, K	P, Kbar	Ref.
1	$(DMET)_2I_3$	0.47	0	72
2	$(DMET)_2IBr_2$	0.58	0	72
3	$(DMET)_2AuCl_2$	0.83	0	73
4	$(DMET)_2AuBr_2$	1.9	0	74
5	κ-$(DMET)_2AuBr_2$	1.0	1.5	75
6	$(DMET)_2Au(CN)_2$	0.86	2.5	76
7	$(DMET)_2AuI_2$	0.55	5.0	73
8	κ-$(MDT\text{-}TTF)_2AuI_2$	3.5	0	71

found among the DMET salts (Table III) with linear anions including $Au(CN)_2$, $AuCl_2$, and $AuBr_2$, which do not form superconducting salts with ET. The appearance of superconductivity in DMET salts has promoted the synthesis of other noncentrosymmetric derivatives of ET. A hybrid of the TTF and BMDT-TTF molecules, (MDT-TTF), forms a superconducting salt with the AuI_2 anion[71] (Table III). It is of interest that neither TTF nor BMDT-TTF give superconducting salts by themselves.

$M(dmit)_2$ AND $M(dddt)_2$ SALTS

All above considered organic superconductors belong to the class of cation radical salts and are synthesized on the base of donors, which are in fact derivatives of only one molecule TTF. The discovery of superconductivity in $M(dmit)_2$ anion radical salts (metal complexes of dimercaptoisotrition) extended the range of molecular superconductors and gave a novel direction to the search. At present five superconductors are known among the $M(dmit)_2$ salts (Table IV).

TABLE IV Molecular superconductors based on $M(dmit)_2$ anion complexes

No.	Salt	T_c, K	P, Kbar	Ref.
1	$TTF[Ni(dmit)_2]_2$	1.6	7.0	77
2	α-$TTF[Pd(dmit)_2]_2$	6.5	20.0	78
3	α'-$TTF[Pd(dmit)_2]_2$	1.7	22.0	78
4	$(CH_3)_4N[Ni(dmit)_2]_2$	5.0	7.0	79
5	$(CH_3)_4N[Pd(dmit)_2]_2$	6.2	6.5	80

They all exhibit superconducting transitions under pressure only. Their structures are characterized by the presence of the $M(dmit)_2$ layers, which alternate with those of cations.[81] The anion layers are formed of the $M(dmit)_2$ stacks with shortened side-by-side S...S contacts. However, despite the presence of such transverse contacts in the layer the electronic structures of these salts are quasi one-dimensional.[82] In particular, detection of the charge density wave instabilities in $TTF[Ni(dmit)_2]_2$ and $TTF[Pd(dmit)_2]_2$ by the X-ray diffuse scattering is the evidence for the such type electronic structure.[83] Further search for this class superconductors is directed to the sulfur substitution for selenium, variations of cations and metals.[81] The finding of superconductivity in $(CH_3)_4N[Ni(dmit)_2]_2$ at low pressure (3.0 kbar) led to the synthesis of new $Ni(dmit)_2$ salts with cations less than $N(CH_3)_4$ to provide conditions for a superconducting transition in these systems at ambient pressure due to the effect of 'chemical compression' of the lattice.[81,84] However, the expectations were not justified, though the $Na[Ni(dmit)_2]_2$ salt was found to be a normal metal down to 25 mK.[84]

Recently a new class of metal complex conductors, $M(dddt)_2$ cation salts in a partially oxidized state, (dddt= 5,6-dihydro-1,4-dithiin-2,3-dithiolate), has been found.[85-87] The $M(dddt)_2$ complexes represent considerable interest, since they belong to dithiolate complexes of the $M(dmit)_2$ type, on one hand. On the other, they are structural modifications of the ET molecule. Formally the central C=C bond of ET is substituted by a metal in the $M(dddt)_2$ complexes (Fig.1). In contrast to the $M(dmit)_2$ complexes, those of $M(dddt)_2$ form conducting cation salts, which are metal complex analogs of ET salts. The $Pt(dddt)_2$ salts with linear anions, *e.g.*, IBr_2, ICl_2, $AuBr_2$, are isostructural to the $(ET)_2IBr_2$ β-phase.[86,87] However, unlike the latter, they are semiconductors due to the $Pt(dddt)_2$ cation dimerization in the stacks. The nature of a counteranion was found to affect much the degree of dimerization, which may be decreased by the choice of an appropriate anion.

$M(dddt)_2$ salts afford a rich potential for their properties to be influenced by variations of anions, metals, heteroatoms, and ligand terminal groups. Recently a new $Ni(dddt)_2$ salt with the HSO_4 anion has been synthesized. This salt retains its metallic state down to 25 K, whereas the structurally identical $(ET)_3(HSO_4)_2$ salt undergoes a metal-insulator transition at much higher temperature of 130 K.[88]

SUPERCONDUCTORS OF THE C_{60} FAMILY

Since cuprate high-temperature superconductors only recently a new sensation has arised in a superconductivity research. Molecular superconductors with sufficiently high T_c based on fullerene (C_{60}) have been discovered. Those are complexes of a new carbon form with some alkaline metals (K_3C_{60}, T_c=18 K[89], Rb_3C_{60}, T_c=30 K[90], $Cs_2Rb_1C_{60}$, T_c = 33 K[91]). A C_{60} molecule has a soccer-ball shape composed of twenty six-member rings faced to twelve five-member rings. In contrast to the discussed above quasi one- and two- dimensional superconductors, the electronic structure of fullerene-based ones has to be three-dimensional. T_c tends to increase at transition from one- to two- and further to three-dimensional systems. Fullerene superconductors open a new promising direction in the field of superconductivity research.

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