

Molecular Conductors Based on $M(\text{dddt})_2$ Bisdithiolene Cation Complexes

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The synthesis, structure and properties of molecular conductors based on $M(\text{dddt})_2$ cation complexes (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) which are metal complex analogs of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) salts are considered. Formally, the central C=C bond of ET is substituted by a metal ion in the $M(\text{dddt})_2$ complexes. The effect of metal ($M = \text{Ni}, \text{Pt}, \text{Pd}$) and counterion on crystal structure and conducting properties of $M(\text{dddt})_2$ complexes is analyzed. The similarity and distinction in structures and properties of $M(\text{dddt})_2$ and ET salts are discussed. © 2002 Elsevier Science (USA)

Key Words: $M(\text{dddt})_2$ complexes; ET salts; Structure; Conductivity; Raman spectra.

1. INTRODUCTION

The first monoanionic complexes $M(\text{dddt})_2$ ($M = \text{Ni}, \text{Pt}, \text{Au}$; dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) were synthesized in the mid-1980 (1–3). These complexes have immediately attracted attention since, on the one hand, they were close to the superconducting bisdithiolene complexes $M(\text{dmit})_2$ (4), and on the other hand, were metal complex analogs of the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) molecule that forms quasi-two-dimensional (2D) superconducting radical cation salts (5). Formally, the central C=C bond of ET is substituted by a metal ion in the $M(\text{dddt})_2$ complexes (Fig. 1). However, it was soon found that in contrast to monoanionic $M(\text{dmit})_2$ complexes which form conducting anion salts in a partially reduced state (4), oxidation of monoanionic $M(\text{dddt})_2$ complexes gives rise to non-conducting neutral ones (3, 6, 7). Interest in the $M(\text{dddt})_2$ complexes newly arose in the early 1990, when it was, for the first time, found that the neutral $M(\text{dddt})_2$ complexes

behave like ET, i.e. form electroconducting cation salts in a partially oxidized state under electrochemical oxidation (8–11). It should be noted that the discovery of stable $M(\text{dddt})_2$ cation salts was unexpected since the neutral complexes have high irreversible (or quasi-reversible) oxidation potentials ($\approx 0.9 \text{ V}$ vs Ag/AgCl) (12). The currently available $M(\text{dddt})_2$ cation salts exhibit the properties from almost insulators to stable metals. In the review the influence of metal and counterion nature on crystal structure and conducting properties of $M(\text{dddt})_2$ cation salts is analyzed.

2. $\text{Ni}(\text{dddt})_2$ CATION SALTS

The first $M(\text{dddt})_2$ cation salt was synthesized unexpectedly when we tried to prepare the $M(\text{dddt})_2$ anion salt in a partially reduced state by electrochemical reduction of neutral $\text{Ni}(\text{dddt})_2$ in the presence of Bu_4NClO_4 as an electrolyte. However, the crystals grew on an anode instead of a cathode. The X-ray analysis of these crystals showed them to be the $M(\text{dddt})_2$ cation salt in a partially oxidized state and have the $[\text{Ni}(\text{dddt})_2]_3(\text{ClO}_4)_2$ (**1**) composition (7, 8, 11). The salt is almost an insulator ($\sigma \cong 10^{-5} \text{ S cm}^{-1}$) as a result of the formation of Ni–S–strongly bonded trimeric cations $[\text{Ni}(\text{dddt})_2]_3^{2+}$ (Fig. 2). The central Ni(1) atom in the trimer has a square-planar configuration which is completed to (4+2) pseudooctahedral one by Ni(1)⋯S interactions. The Ni(2) atom and its symmetric equivalent Ni(2a) are pentacoordinated. The presence of considerably shortened Ni⋯S contacts (2.659 Å and 3.055 Å) evidences for strong interaction between the monomeric $M(\text{dddt})_2$ units in the trimer. Whereas the metal-metal- or metal-sulfur-bonded dimers of bisdithiolenes are widely known (13), the formation of metal-sulfur-bonded trimeric bisdithiolene was first found. The $[M(\text{dddt})_2]_3^{2+}$ trimers are packed in stacks in the crystals of the salt **1** (8, 11). There are no intertrimer shortened contacts in the stacks, whereas there are shortened side-by-side S⋯S contacts (3.36–3.66 Å) between the stacks as in the ET salts.

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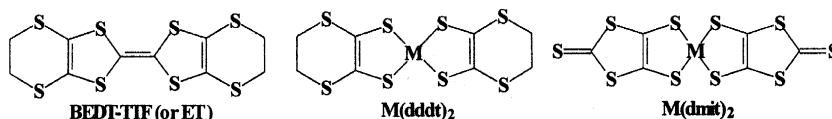


FIG. 1. Structural formulae of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) and metal bisdithiolates $M(\text{dddt})_2$ and $M(\text{dmit})_2$.

The finding of Ni–S–strongly bonded trimeric cation in $[\text{Ni}(\text{dddt})_2]_3(\text{ClO}_4)_2$ stimulated the synthesis of the $\text{Ni}(\text{dddt})_2$ salts with other tetrahedral anions aimed at the search for polymeric bisdithiolene complexes with (4+2) Ni coordination. The possibility of the existence of such type polymeric complexes was also predicted theoretically (13). However, the attempts to obtain coordination polymers based on the $\text{Ni}(\text{dddt})_2$ cation complexes by varying counterions turned to be unsuccessful yet. In contrast to $[\text{Ni}(\text{dddt})_2]_3(\text{ClO}_4)_2$, no shortened Ni...S contacts were found in the structures of the $\text{Ni}(\text{dddt})_2$ salts of the same stoichiometry (3:2) with the other tetrahedral anions (BF_4 (2), HSO_4 (3), HSeO_4 (4)) (9, 14–16). The stacks in 2–4 are subdivided into the $[\text{Ni}(\text{dddt})_2]_3$ triads depending on the overlapping mode between the cations. Unlike $(\text{ET})_3X_2$ salts with the same tetrahedral anions (X) which are isostructural, 1 and 2 are isostructural neither to each other nor to the similar ET salts, whereas 3 and 4 are isostructural to the latter. 2 is a semiconductor, 3 and 4 exhibit a metal-to-insulator (M–I) transition. Though the internal structures of the cation stacks and layers are very similar in the $\text{Ni}(\text{dddt})_2$ and ET salts with the HSO_4 and HSeO_4 anions, their conducting properties are essentially different (16). For the ET salts, the substitution of the HSO_4 anion by the larger HSeO_4 one results in the shift of

the metal-to-insulator transition temperature to a higher value (130 K \rightarrow 180 K), whereas it remains almost unchanged in the $\text{Ni}(\text{dddt})_2$ salts (~ 30 K) (Fig. 3). The decrease of the transition temperature in the isostructural ET salts could be a result of compression of the crystal lattice (i.e., a chemical pressure effect) when passing from $(\text{ET})_3(\text{HSeO}_4)_2$ to $(\text{ET})_3(\text{HSO}_4)_2$. However, this effect is not observed in isostructural $[\text{Ni}(\text{dddt})_2]_3(X)_2$ ($X = \text{HSO}_4, \text{HSeO}_4$). The difference in the conducting properties of the isostructural ET and $\text{Ni}(\text{dddt})_2$ salts, most probably, originates from variations in their electronic structures (16, 17). The reason is that whereas only HOMO of ET plays a role in the conduction bands of its salts, both HOMO and LUMO of $M(\text{dddt})_2$ complexes can be involved in those of their salts. The lack of the chemical pressure effect in the $\text{Ni}(\text{dddt})_2$ salts (3,4) probably originates from a stiffer nature of the lattice of the $M(\text{dddt})_2$ ones as compared with the ET salts as a result of the occurrence of weak additional $M \cdots S$ bonding interactions (16). It should be noted that unlike the parent $\text{Ni}(\text{dddt})_2$ and ET salts with HSO_4 anion, the mixed salt

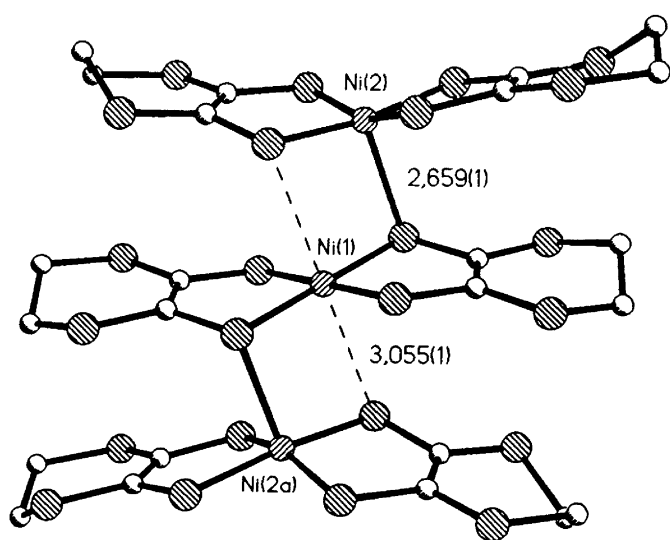


FIG. 2. The geometry of the trimeric $[\text{Ni}(\text{dddt})_2]_3^{2+}$ cation in $[\text{Ni}(\text{dddt})_2]_3(\text{ClO}_4)_2$.

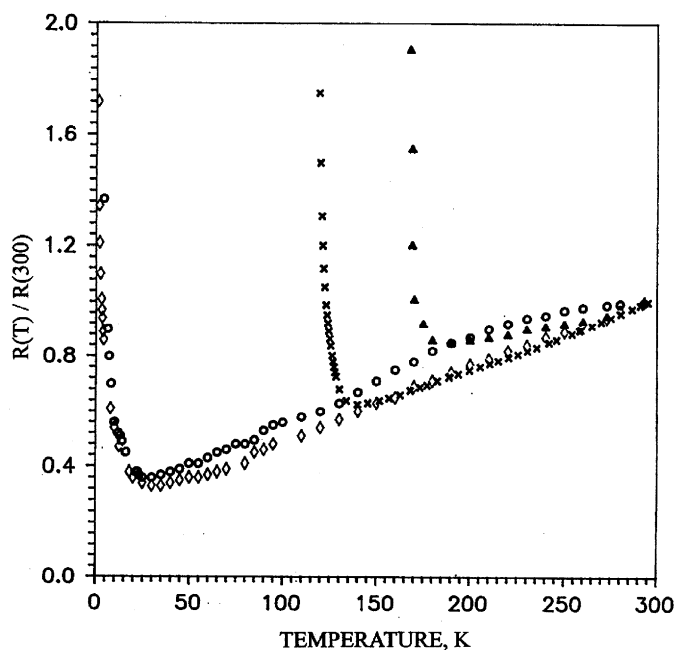


FIG. 3. Temperature dependence of the resistivity for crystals of $(\text{ET})_3X_2$, $X = \text{HSO}_4$ (\times), HSeO_4 (\blacktriangle), and $[\text{Ni}(\text{dddt})_2]_3X_2$, $X = \text{HSO}_4$ (\diamond), HSeO_4 (\circ).

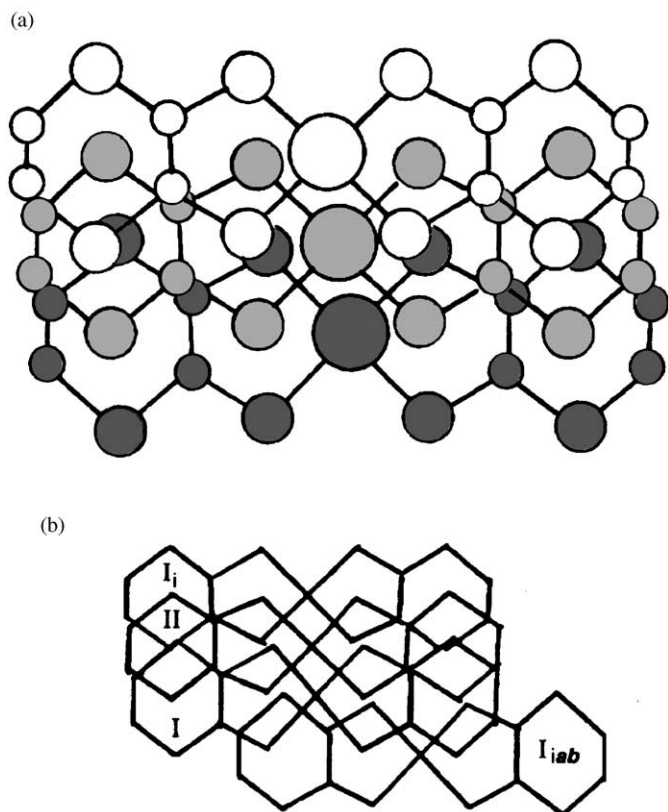


FIG. 4. Modes of overlap in $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ (a) and $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ (b).

$\{[\text{ET}]_{1-x}[\text{Ni}(\text{dddt})_2]_x\}_3(\text{HSO}_4)_2$ ($x = 0.42 \pm 0.03$) exhibits a semiconducting temperature dependency of resistivity (16). Such behavior is, most probably, a result of electronic localization in the mixed cation layers because ET and $\text{Ni}(\text{dddt})_2$ have considerably different redox potentials.

The discovery of conducting properties of the $\text{Ni}(\text{dddt})_2$ cation salts with tetrahedral anions impelled the synthesis of the $\text{Ni}(\text{dddt})_2$ salts with anions of different geometry. In this connection, of particular interest are linear anions with most of which ET forms metallic and superconducting salts (5). When $\text{Bu}_4\text{NAuBr}_2$ was used as an electrolyte, the salt $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ was obtained by electrocrystallization (18). The X-ray analysis showed that unlike the $\text{Ni}(\text{dddt})_2$ salts with the tetrahedral anions, the conducting layers in the $\text{Ni}(\text{dddt})_2$ salt of the same stoichiometry (3:2) with the linear AuBr_2 anion are built up of the $\text{Ni}(\text{dddt})_2$ uniform stacks (Figs. 4 and 5) (18). With respect to conducting properties, $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ is a quasi-2D molecular metal stable down to at least 1.3 K (Fig. 6). The resistivity anisotropy is almost absent in the plane of the cation sheets (the ac plane), while ρ_b/ρ_{ac} is equal to ~ 600 at $T = 300$ K and is close to the anisotropy of quasi-2D metals based on the ET salts. It should be noted that unlike ET, $\text{Ni}(\text{dddt})_2$

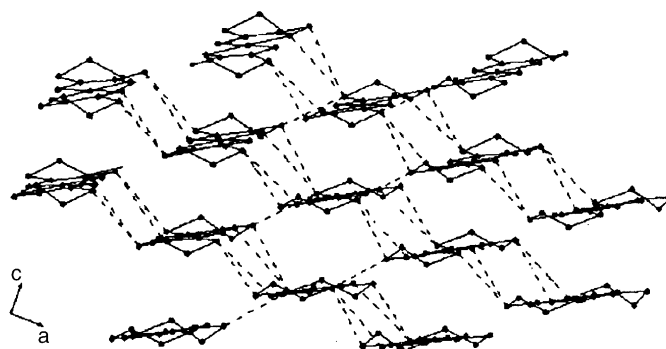


FIG. 5. Arrangement of cations in the conducting layer of $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$. The dashed lines correspond to shortened interstack side-by-side $\text{S}\cdots\text{S}$ contacts.

does not form salts with other linear anions (I_3 , AuI_2). The electrolytes containing these anions decompose during electrocrystallization that is associated with the high oxidation potential of $[\text{Ni}(\text{dddt})_2]^0$. The use of $\text{Bu}_4\text{NAgBr}_2$ as a supporting electrolyte yields the $[\text{Ni}(\text{dddt})_2]_3\text{Ag}_x\text{Br}_y$ salt ($x \cong 2.5$; $y \cong 3$) (19). This salt is close to the ET one ($(\text{ET})\text{Ag}_{2.4}\text{Br}_3$) in the anion composition. The latter is formed as a result of electrochemical oxidation of ET in the presence of the same electrolyte (20). Relatively low quality of the crystals did not allow the full structure of the $\text{Ni}(\text{dddt})_2$ salt to be solved. However, one could assume that the anion sheet has a polymeric structure as it occurs in the ET salt (20). The $\text{Ni}(\text{dddt})_2$ one exhibits a resistive hump at ~ 60 K, but remains metallic down to 4.2 K (19).

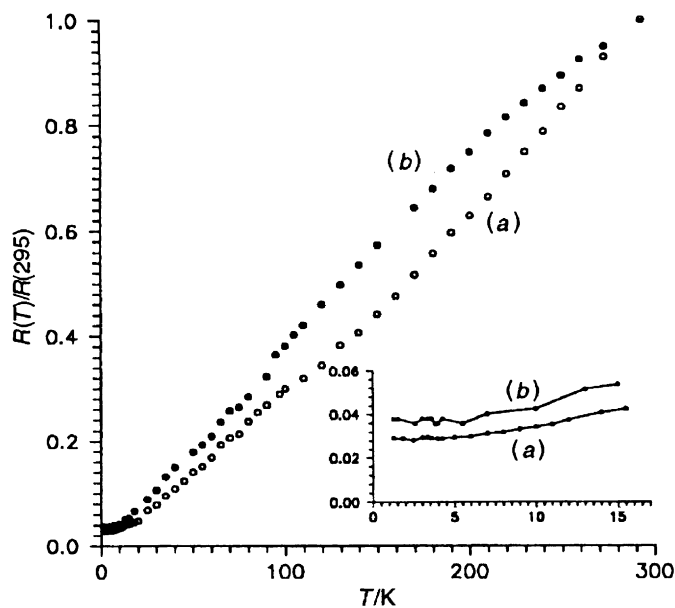


FIG. 6. Temperature dependences of the resistivity of $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ along the a and b axes (18).

3. $\text{Pt}(\text{DDDT})_2$ AND $\text{Pd}(\text{DDDT})_2$ CATION SALTS

The known $\text{Pt}(\text{dddt})_2$ and $[\text{Pd}(\text{dddt})_2]$ salts with different linear, tetrahedral and octahedral anions are semiconductors (Sc, 1–18, Table 1). The salts have the layered structure in which the $\text{Pd}(\text{Pt})(\text{dddt})_2$ cation layers alternate with those composed of inorganic anions. The conducting layers consist of the $\text{Pd}(\text{Pt})(\text{dddt})_2$ stacks with the shortened side-by-side $\text{S}\cdots\text{S}$ contacts. The feature of the crystal structure of the $\text{Pd}(\text{Pt})(\text{dddt})_2$ salts with linear, tetrahedral and octahedral anions is the presence of the metal-metal-bonded dimers of $\text{Pt}(\text{dddt})_2$ or $\text{Pd}(\text{dddt})_2$ in the cation stacks (Fig. 7). Dimerization is probably associated with the Pt and Pd ability to form metal-metal bonds in contrast to Ni. The cations in the dimers are arranged face-to-face and the $M-M$ distances are equal to 3.0–3.3 Å depending on the anion. Though the $\text{Pt}(\text{dddt})_2$ and $\text{Pd}(\text{dddt})_2$ salts with the linear IBr_2 , ICl_2 , AuBr_2 anions have the same stoichiometry (2:1) as metallic and superconducting β -ET salts with these anions and their layered crystal structures are similar, the former is a semiconductor unlike the latter as a result of the $\text{Pt}(\text{Pd})(\text{dddt})_2$ strong dimerization in the stacks (10, 11, 21, 23).

Since $\text{Pd}(\text{Pt})(\text{dddt})_2$ cations tend to forming dimers, one could expect them to form salts with the κ -type structure of a cation layer characteristic of the ET-based superconductors with $T_c \geq 10$ K. The cation sheets in these superconductors are built up of orthogonally arranged ET dimers with the shortened side-by-side $\text{S}\cdots\text{S}$ contacts (5). Though the efforts to prepare the κ -type $\text{Pd}(\text{Pt})(\text{dddt})_2$

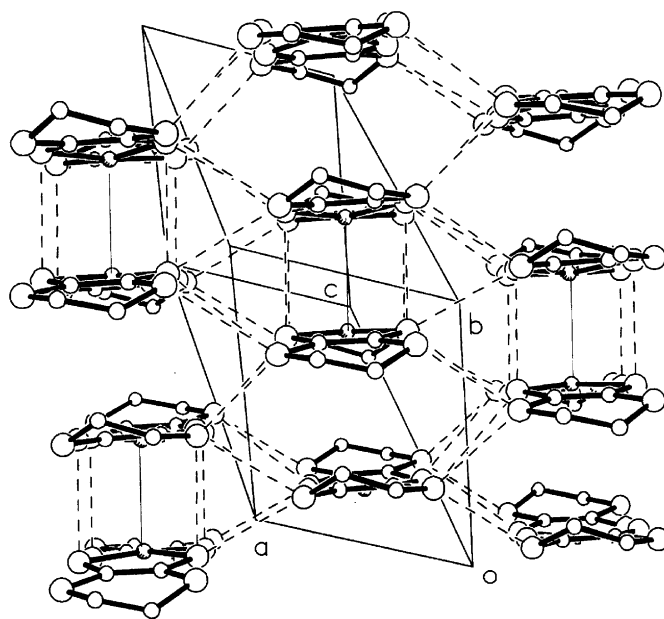


FIG. 7. Dimeric packing of the $\text{Pd}(\text{dddt})_2$ cation in $[\text{Pd}(\text{dddt})_2]_2\text{CF}_3\text{SO}_3$.

TABLE 1
Cation Salts of $\text{Pt}(\text{dddt})_2$ and $\text{Pd}(\text{dddt})_2$

Compound	$\sigma_{\text{RT}}(\text{S cm}^{-1})$	σ vs T	Reference
1 $[\text{Pt}(\text{dddt})_2]_2\text{AuBr}_2$	0.5–1.0	Sc	(10, 11, 21)
2 $[\text{Pt}(\text{dddt})_2]_2\text{IBr}_2$	5–10	Sc	(10, 11, 21)
3 $[\text{Pt}(\text{dddt})_2]_2\text{ICl}_2$	5–10	Sc	(10, 11, 21)
4 $[\text{Pt}(\text{dddt})_2]_3(\text{BF}_4)_2$	0.5–1.0	Sc	(11)
5 $[\text{Pt}(\text{dddt})_2]_2\text{FeCl}_4$	0.1–1.0	Sc	(22)
6 $[\text{Pd}(\text{dddt})_2]_2\text{AuBr}_2$	2.0	Sc	(19, 23)
7 $[\text{Pd}(\text{dddt})_2]_2\text{IBr}_2$	0.5–1.0	Sc	(19)
8 $[\text{Pd}(\text{dddt})_2]_x\text{ClO}_4$	4×10^{-2}	Sc	(19)
9 $[\text{Pd}(\text{dddt})_2]_x\text{BF}_4$	2×10^{-3}	Sc	(19)
10 $[\text{Pd}(\text{dddt})_2]_x\text{ReO}_4$	6×10^{-3}	Sc	(19)
11 $[\text{Pd}(\text{dddt})_2]_x\text{InCl}_4$	3×10^{-1}	Sc	(19)
12 $[\text{Pd}(\text{dddt})_2]_x\text{ZnCl}_4$	4.0	Sc	(19)
13 $[\text{Pd}(\text{dddt})_2]_2\text{CF}_3\text{SO}_3$	1.0	Sc	(24)
14 $[\text{Pd}(\text{dddt})_2]_2\text{GaBr}_4$	0.25	Sc	(25)
15 $[\text{Pd}(\text{dddt})_2]_x\text{CdCl}_4$	1.0	Sc	(19)
16 $[\text{Pd}(\text{dddt})_2]_2\text{PF}_6$	1.0	Sc	(19)
17 $[\text{Pd}(\text{dddt})_2]_2\text{SbF}_6$	1–2	Sc	(19)
18 $[\text{Pd}(\text{dddt})_2]_2\text{AsF}_6$	1.0	Sc	(19)
19 $[\text{Pd}(\text{dddt})_2]_2\text{SnCl}_5$	1.0	$T_{\text{M-I}} \cong 140$ K	(19)
20 $[\text{Pd}(\text{dddt})_2]_2\text{TeCl}_5$	11–25	$\sigma_{\text{RT}} \cong \sigma_{4.2}$	(19)
21 $[\text{Pd}(\text{dddt})_2]_2\text{Ag}_{1.54}\text{Br}_{3.5}$	15–40	M	(26)

salts by varying anions were unsuccessful so far, the search resulted in the synthesis of the $\text{Pd}(\text{dddt})_2$ salts with metal-like behavior of conductivity (19–21, Table 1). Among these salts the most interesting is $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ that was synthesized by the electrochemical oxidation of $[\text{Pd}(\text{dddt})_2]^0$ in the presence of $\text{Bu}_4\text{NAgBr}_2$ as an electrolyte. The salt exhibits a metallic behavior of conductivity down to 1.3 K (26). The crystal structure of $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ contains alternating layers of donor-cations and non-stoichiometric silver bromide complex anions. The Ag and Br atoms of the anion layer are disordered occupying four and six positions, with total populations of 1.54(5) and 3.50(1), respectively. The conducting cation layers are formed of the $\text{Pd}(\text{dddt})_2$ uniform stacks with the shortened side-by-side $\text{S}\cdots\text{S}$ contacts between the stacks. The structure of the $\text{Pd}(\text{dddt})_2$ stacks is similar to that of $\text{Ni}(\text{dddt})_2$ ones in metallic $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ (Figs. 4a and 5). Since Pd and Pt bisdithiolates usually form dimers inside the stacks of their charge transfer salts, the existence of the uniform $\text{Pd}(\text{dddt})_2$ chains in the present salt is quite remarkable. Of principal importance in studying the properties of $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ were problems associated with charge state of $\text{Pd}(\text{dddt})_2$ and oxidation state of Ag. The metallic behavior of conductivity together with the band structure calculations testified to that charge of $\text{Pd}(\text{dddt})_2$ would be close to +0.5 (26). The measurements of the Raman spectra for the $M(\text{dddt})_2$ complexes in different charge state confirmed this conclusion (27). It has been found that the C=C vibration frequency gradually decreases and the C-S frequency gradually increases with

a decreasing number of valence electrons in the $M(\text{dddt})_2$ ($M = \text{Ni, Pd, Pt, Au}$) complexes. This finding shows that the oxidation and reduction take place primarily on the dddt ligand and electronic configuration of metal d^8 ($M = \text{Ni, Pd, Pt, Au}$) does not change at the formation of charge transfer compounds of the $M(\text{dddt})_2$ complexes (27). There is a linear correlation between the C=C frequency and average charge on each dddt ligand ($-n$), (Fig. 8), which is well described by the equation: $\nu_1(\text{cm}^{-1}) = 1183 + 169n$ (n is positive). According to this equation, the C=C frequency (1301 cm^{-1}) for the $[\text{Pd}(\text{dddt})_2] \text{Ag}_{1.54}\text{Br}_{3.50}$ salt corresponds to $n = 0.7$, which gives charge of $+1.88$ on silver (27). Recent study of magnetic properties of the salt by the EPR method evidenced the presence of the Ag^{2+} cations. Two signals are observed in the EPR spectrum: one is due to the conduction electrons of the $\text{Pd}(\text{dddt})_2$ cation layers and the other is attributed to localized magnetic moments of Ag^{2+} in the anion layers (28). Oxidation of the electrolyte $\text{Bu}_4\text{NAgBr}_2$ ($\text{Ag}^{1+} \rightarrow \text{Ag}^{2+}$) during electrocrystallization of $[\text{Pd}(\text{dddt})_2] \text{Ag}_{1.54}\text{Br}_{3.5}$ occurs due to a high oxidation potential of $[\text{Pd}(\text{dddt})_2]^0$. However, the formation of the silver ($2+$) bromide complex anion was unexpected since electrochemical oxidation of $[\text{Ni}(\text{dddt})_2]^0$ as well as ET in the presence of the same electrolyte yields the salts containing the silver ($1+$) bromide complex anion.

4. CONCLUSION AND PERSPECTIVE

The metal (M) and counterion nature strongly affect the crystal structure and conducting properties of the $M(\text{dddt})_2$ cation salts in a partially oxidized state, modifying their

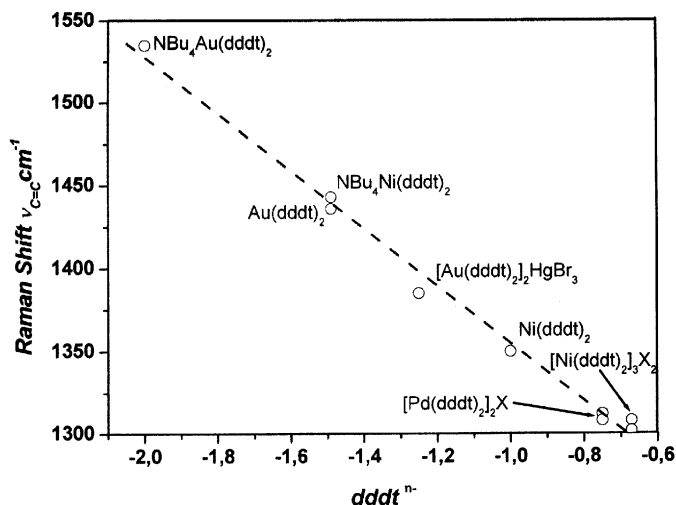


FIG. 8. The totally symmetric C=C vibration frequency against the charge ($-n$) of the dddt^{n-} ligand based on Au^{3+} (d^8) and M^{2+} (d^8) ($M = \text{Ni, Pd, and Pt}$) formalism showing a linear correlation. $[\text{Ni}(\text{dddt})_2]_3\text{X}_2$ ($X = \text{HSO}_4, \text{ClO}_4$), $[\text{Pd}(\text{dddt})_2]_2\text{X}$ ($X = \text{PF}_6, \text{SbF}_6, \text{AuBr}_2$) (27).

properties from almost dielectric to stable metals. The $M(\text{dddt})_2$ salts ($M = \text{Ni, Pd}$) in which the cation layers consist of the $M(\text{dddt})_2$ uniform stacks with the shortened side-by-side S...S contacts are stable quasi-2D molecular metals. Though the crystal structures of the $M(\text{dddt})_2$ and ET salts are similar, their electronic band structures and some properties are essentially different.

1. For the $M(\text{dddt})_2$ complexes, the energy gap between HOMO and LUMO is small ($\sim 0.4 \text{ eV}$), while in ET LUMO lies considerably higher in energy than HOMO ($\sim 2 \text{ eV}$) (21). Only HOMO of ET plays a role in the conduction bands of its salts, whereas both HOMO and LUMO of the $M(\text{dddt})_2$ complexes can be involved in those of their salts.

2. As compared to ET, the neutral $M(\text{dddt})_2$ complexes are very poorly soluble in organic solvents thus making difficulties in preparing crystals of their salts by electrocrystallization. Low solubility of the complexes is probably associated with the intermolecular $\pi-d$ interaction between S and metal atoms.

3. Oxidation potentials for the neutral $M(\text{dddt})_2$ complexes ($\sim 0.9 \text{ V}$) are considerably higher than those for the ET molecule ($\sim 0.5 \text{ V}$) that limits a number of anions to be used as counterions in the synthesis of the $M(\text{dddt})_2$ cation salts.

4. Polymorphism characteristic of the ET salts is not observed in the $M(\text{dddt})_2$ cation salts that is probably associated with a stiffer nature of the lattice of these salts as compared to the ET ones.

There are many possibilities of widening a family of molecular conductors based on the $M(\text{dddt})_2$ cation complexes by varying metal, anion, and modifying the dddt ligand itself. In this aspect of great interest is the synthesis of cation salts based on $\text{Au}(\text{dddt})_2$, which has the κ -type packing and is isostructural to the ET molecule in contrast to the neutral isostructural $\text{Ni}(\text{Pt}(\text{Pd}))(\text{dddt})_2$ complexes (3, 6, 7, 29). Though it has already been reported on the synthesis of several conducting cation salts of $\text{Au}(\text{dddt})_2$ (9, 11), the data about their structures are completely lacking. In the context of chemical modification of $M(\text{dddt})_2$ system, the nickel complexes of 5,6-dihydro-1,4-dithiin-2,3-diselenolate ligand (ddds) were synthesized (30). It is interesting that neutral $\text{Ni}(\text{ddds})_2$ is not isostructural to $\text{Ni}(\text{dddt})_2$ and has a dimeric structure due to the Ni-Se [2.496 \AA] bonds (30). However, the cation salts of $\text{Ni}(\text{ddds})_2$ have not been obtained probably due to very low solubility of neutral $\text{Ni}(\text{ddds})_2$. It should be noted that this result was not unexpected since the substitution of S for Se in the tetrachalcogenfulvalene family gives rise to significantly lower solubility and higher oxidation potentials. In respect of chemical modification of $M(\text{dddt})_2$ systems, the synthesis of metal complexes based on the oxygen analog of dddt containing the O atom instead of S in 1,4-positions (dodt) would be more preferable. As

compared to the $M(\text{dtdt})_2$ complexes, the $M(\text{dodt})_2$ ones must be more soluble and have lower oxidation potentials. It is known that the ET oxygen analog, namely, (BEDO) has essentially higher solubility and lower oxidation potential than ET.

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