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# Molecular (super)conductors derived from bis-dithiolate metal complexes

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## Abstract

The synthesis, electrochemical behavior, electrocrystallization and solution diffusion preparation of the $M(dmit)_2$ bis-dithiolate metal complexes ($dmit^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolato) and derived non integral oxidation state compounds is briefly recalled. The properties of the eight superconductors known in this series, namely, $[TTF][Ni(dmit)_2]_2$, $[Me_4N]_{0.5}[Ni(dmit)_2]$, $\alpha$-$[TTF][Pd(dmit)_2]_2$, $\alpha'$-$[TTF][Pd(dmit)_2]_2$, $\beta$-$[Me_4N]_{0.5}[Pd(dmit)_2]$, $[Me_2Et_2N]_{0.5}[Pd(dmit)_2]$, $\alpha$-$[EDT\text{-}TTF][Ni(dmit)_2]_2$, and $\beta'$-$[Me_2Et_2P]_{0.5}[Pd(dmit)_2]$, (TTF = tetrathiafulvalene, EDT-TTF = ethylenedithio-tetrathiafulvalene) are described, including crystal structures, conductivities, IR/Raman studies, temperature/pressure phase diagrams, observation of charge density waves, and band structure calculations. The enlargement of

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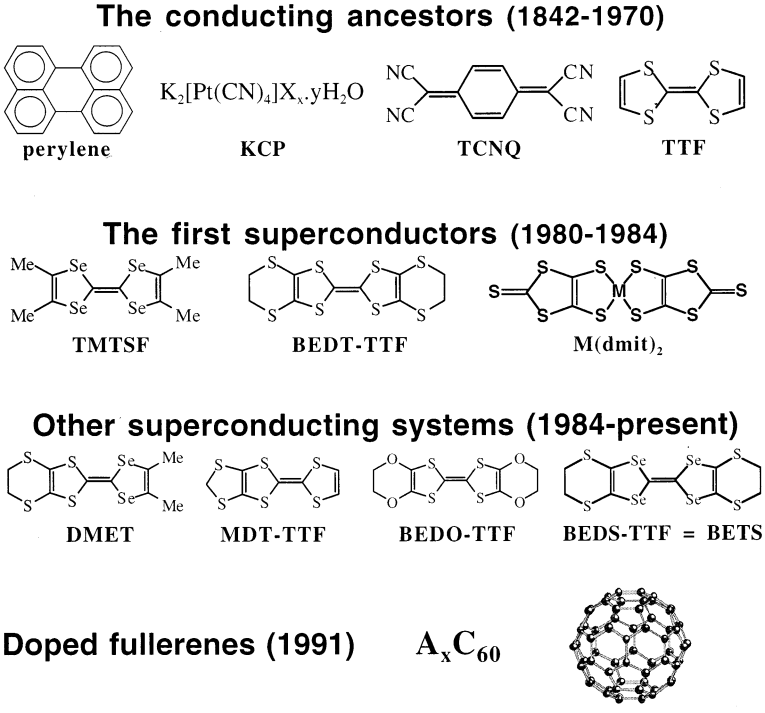
this series of conducting compounds, not only by modification of the inorganic countercation or the organic cation radical, but also by modification of the dmit ligand itself, is reviewed, but superconductivity seems to be restricted to the dmit-based systems. The studies on these conducting bis-dithiolate metal compounds have been extended to other properties and utilization, such as, for example, conducting Langmuir-Blodgett films, unconventional magnetic properties, and nonlinear optics (NLO). Recent tentative research works on the interplay of conducting, magnetic and NLO properties in such compounds are reported.

*Keywords:* Metal bis-dithiolate metal complexes; 2-Thioxo-1,3-dithiole-4,5-dithiolato; Conductivity; Superconductivity; Magnetism; Nonlinear optics

## 1. Introduction

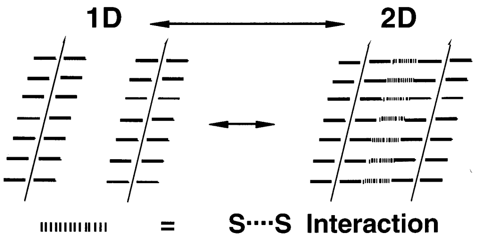
Molecule-based solids usually exhibit physical properties similar to that of the isolated molecule. In a few cases, they also exhibit properties which are distinct from those of the isolated molecules, including electrical, optical and magnetic properties. In even fewer cases, they exhibit cooperative properties such as superconductivity and ferromagnetism.



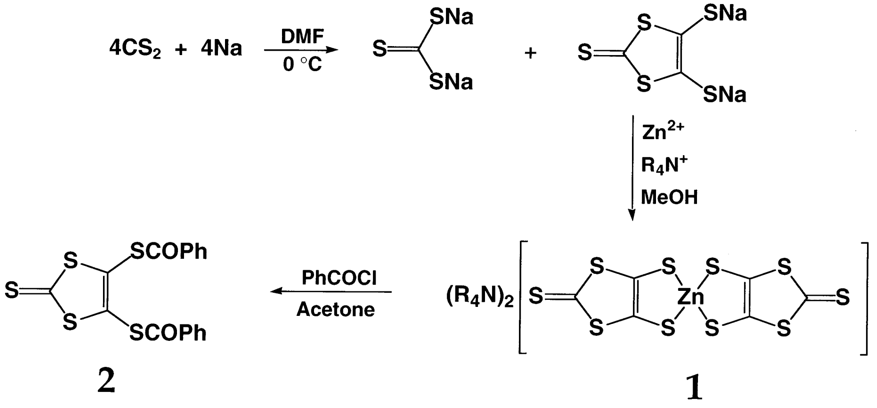
(1)

As far as electrical conductivity is concerned, the molecule-based conducting 'ancestors' are salts of perylene firstly described in 1960 [1] (Chart 1), partially oxidized tetracyanoplatinate salts (such as KCP, prepared for the first time in 1842 [2], but characterized in 1968 [3], and identified as a conductor only in 1972 [4]), and salts of TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) [5] and of TTF (tetrathiafulvalene) [6], including the now famous (TTF)·(TCNQ) adduct [7]. Metal-like conductivity was first reported for KCP [3], (*N*-methylphenazenium)(TCNQ) [8], and (TTF)·(TCNQ) [7].

Following these seminal results, a large number of molecule-based conductors were prepared and studied. Their structure shows a common feature, one-dimensionality (1-D), i.e. a stacking along one direction of the molecular units with intermolecular interaction along the stacks and none between the stacks (Scheme 1). All 1-D systems were predicted by Peierls to undergo metal-to-insulator transition at low temperatures [9]. Yet, superconductivity was first observed in salts derived from TMTSF (tetramethyltetraselenafulvalene) [10], BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) [11], and M(dmit)$_2$ [12]. This article will concentrate on molecular (super)conductors derived from bis-dithiolate metal complexes, and especially the M(dmit)$_2$ systems. The BEDT-TTF compounds are the subject of a second article within this issue [13]. To date, more than a hundred molecule-based superconductors have been described (which is not that many) and are mostly salts derived from organic donor molecules, including those derived from BEDS-TTF (bis(ethylenedithio)tetraselenafulvalene usually designated BETS) which form the subject of a third article [14]. It is interesting to note that these systems, in which superconductivity has been observed, also share a common structural feature: they are no longer 1-D, but exhibit interaction between molecules of adjacent stacks often related to chalcogen–chalcogen close contacts. Thus, they can be described as 2-D (or at least quasi 1-D) systems (see Scheme 1). Dimensionality and theoretical aspects on these systems will be discussed in a fourth article within this issue [15]. Recently, another series of molecule-based superconductors which could be described as 3-D, i.e. the doped $C_{60}$ fullerenes have been discovered [16], and such systems will be described in a fifth article [17].



Scheme 1.



Scheme 2.

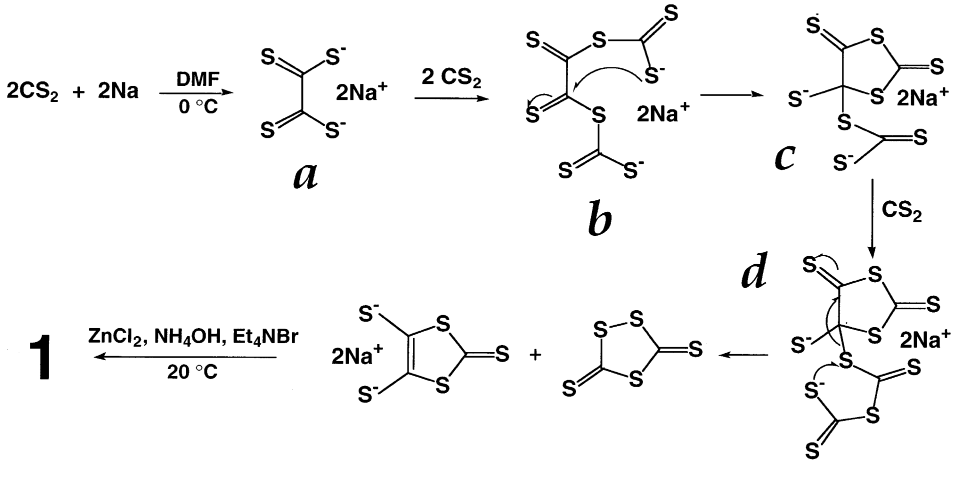
## 2. Preparation of M(dmit)$_2$ complexes and derived salts

The dmit ligand (2-thioxo-1,3-dithiole-4,5-dithiolato) is prepared by reducing $CS_2$ with sodium in dimethylformamide (Scheme 2) [18]. To separate and stabilize the rather unstable sodium salt of the dmit ligand ($C_3S_5Na_2$) from the sodium trithiocarbonate salt ($CS_3Na_2$), the derived stable zinc complex **1**, $[R_4N]_2[Zn(dmit)_2]$, is prepared. A further way to protect the dmit ligand consists of treating complex **1** with benzoyl chloride which gives the stable 4,5-bis(benzoylthio)-1,3-dithiol-2-thione **2**, dmit(COPh)$_2$, which can be conveniently stored and used as a precursor for further work.

Quite recently, Bryce et al. reported an alternate, more efficient route for preparing complex **1** [19]. This method consists of using in the first steps a large excess of $CS_2$ versus sodium, upon which either a large portion of the trithiocarbonate salt is converted into the sodium salt of dmit, or a different mechanism is operating. The proposed mechanism is depicted in Scheme 3 and involves the reaction of two equivalents of $CS_2$ on the intermediate ***a***, possibly affording dithiolate ***b***. Intramolecular cyclization of ***b*** could give isomer ***c***. Reaction of ***c*** with a further one equivalent of $CS_2$ could yield dithiolate ***d***. Fragmentation of ***d*** affords the desired sodium salt of dmit which is converted in situ into the zinc complex **1**. Whether this mechanism is valid is after all not that important, as long as the yields which have been claimed, and that we checked up, are twice as high.

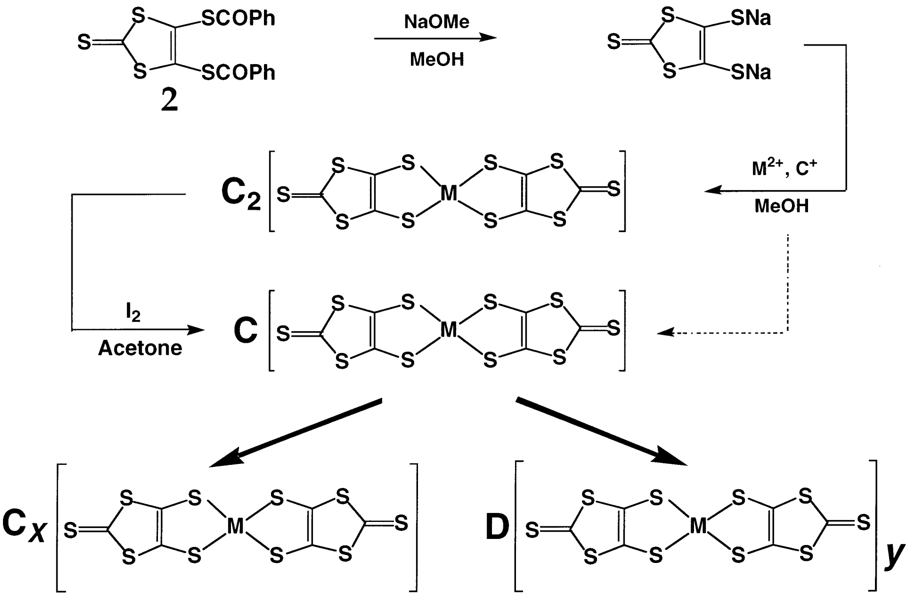
When needed the dmit$^{2-}$ anion could be regenerated from the thioester **2** by treatment with sodium methoxide and directly reacted in situ with a salt of the appropriate metal M and a salt of the appropriate cation C, typically a tetraalkylammonium salt, to afford in most cases the desired $[C]_2[M(dmit)_2]$ (Scheme 4).

In some cases, it may even be convenient to isolate the highly reactive Na$_2$dmit salt by precipitation from diethyl ether using standard Schlenk techniques. This method allows not only very clean further synthesis but also synthesis in which high pH values of the reaction mixture would prohibit the precipitation of the desired



Scheme 3.

complex. A number of $[C]_2[M(dmit)_2]$ complexes ($C = H_4N^+$, $R_4N^+$, $R_4As^+$, $R_4P^+$ and $Me_3SO^+$; $n = 2, 1, 0$; M = Ni, Pd, Pt, Fe, Cu, Au and Rh) have been prepared [12a]. The corresponding monoanionic salts $[C][M(dmit)_2]$ are generally obtained from the dianionic salt by iodine oxidation. However, in some cases, the monoanionic salt can be directly obtained from $Na_2dmit$.



Scheme 4.

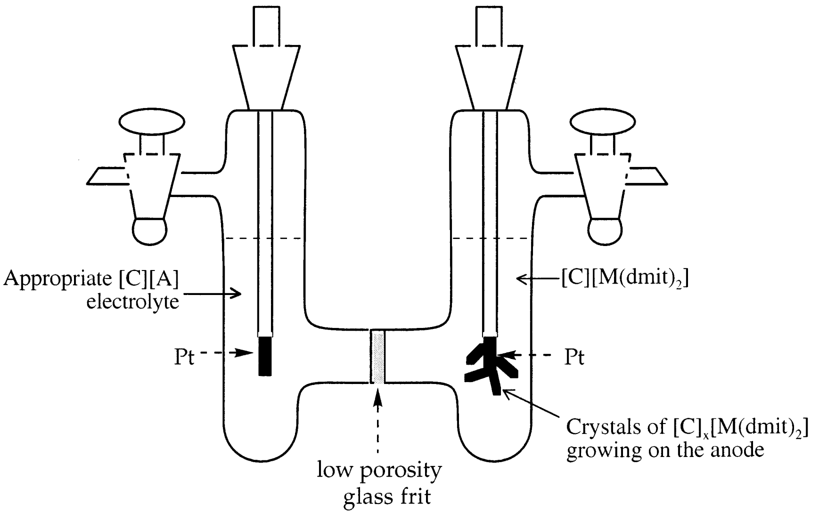


Fig. 1. Electrolysis cell.

Two kinds of electron transfer salts may be obtained: (i) the cation-deficient $[C]_x[M(dmit)_2]$ non-integral oxidation state complexes, and (ii) the donor-acceptor $[D][M(dmit)_2]_y$ compounds in which D is an appropriate donor molecule. These electron transfer salts can be prepared by either electrocrystallization or by metathesis reaction. Typically, when using the electrocrystallization method, solutions of the appropriate $[C][M(dmit)_2]$ precursor complex, and sometimes of an appropriate salt of the C cation (to increase solubility and conductivity of the solutions), in an organic solvent are placed in both compartments, separated by a frit, of a H- or U-shaped cell (Fig. 1).

The electrodes (mostly platinum) are then inserted in both compartments, and, in order to control the crystal growth rate, galvanostatic electrolysis involving current intensities in the 0.1–5 μA range is generally preferred to potentiostatic electrolysis. The crystals are grown on the anode according to the reaction shown in (Eq. (1)):

$$n[C][M(dmit)_2] \rightarrow \{[C]_x[M(dmit)_2]\}_n + n(1-x)C^+ + n(1-x)e^- \qquad (1)$$

A number of non-integral oxidation state complexes, $[C]_x[M(dmit)_2]$, have been produced by electrochemical (or simple chemical) oxidation [12]. Most of them exhibit semiconducting behavior, or metal-like behavior, but four phases (see below, Table 1) undergo a superconducting transition.

The half-wave redox potential of the electrochemical couple $[M(dmit)_2]^{-1}/[M(dmit)_2]^0$ can be estimated around 0.2 V (versus SCE) [20]. Thus, the $M(dmit)_2$ complexes can be considered as moderate acceptors and used in combination with appropriate donor molecules for preparing donor–acceptor complexes in which partial charge-transfer may be anticipated. A number of $[D][M(dmit)_2]_y$ donor–acceptor compounds have been also obtained with various D donor molecules such as TTF, TMTSF, BEDT-TTF and related molecules, and various stoichiometry, $y$

Table 1
List of molecular superconductors derived from $M(dmit)_2$ complexes

| Number | Compound | Year | $T_c$ (K) | $P$ (kbar) | Ref. |
|---|---|---|---|---|---|
| **1** | $[TTF][Ni(dmit)_2]_2$ | 1986 | 1.62 | 7 | [21] |
| **2** | $[Me_4N]_{0.5}[Ni(dmit)_2]$ | 1987 | 5 | 7 | [22] |
| **3** | $\alpha'$-$[TTF][Pd(dmit)_2]_2$ | 1989 | 5.93 | 24 | [23] |
| **4** | $\alpha$-$[TTF][Pd(dmit)_2]_2$ | 1990 | 1.7 | 22 | [24] |
| **5** | $\beta$-$[Me_4N]_{0.5}[Pd(dmit)_2]$ | 1991 | 6.2 | 6.5 | [25] |
| **6** | $[Me_2Et_2N]_{0.5}[Pd(dmit)_2]$ | 1992 | 4 | 2.4 | [26] |
| **7** | $\alpha$-$[EDT\text{-}TTF][Ni(dmit)_2]$ | 1993 | 1.3 | Ambient | [27] |
| **8** | $\beta'$-$[Et_2Me_2P]_{0.5}[Pd(dmit)_2]$ | 1998 | 4 | 6.9 | [28] |

being mostly equal to 2 [12]. These $[D][M(dmit)_2]_y$ compounds can be either chemically or electrochemically prepared. In the first case, the $[M(dmit)_2]^0$ neutral complex being often available with difficulty, direct reaction between the neutral donor and acceptor components was not possible. Thus, the metathesis reaction (Eq. (2)) between the appropriate $D^+$ and the $[M(dmit)_2]^{-1}$ salts was used:

$$nD^+ + ny[M(dmit)_2]^{-1} \rightarrow \{[D][M(dmit)_2]_y\}_n \quad (2)$$

Good quality crystals were generally obtained by slow interdiffusion of solutions of both salts in the diffusion cell shown in Fig. 2.

The $[D][M(dmit)_2]_y$ compounds can also be prepared using electrocrystallization techniques similar to those employed in the case of the $C_x[M(dmit)_2]$ complexes. In this case, the $D^+$ species is first generated in the anodic compartment (Eq. (3)):

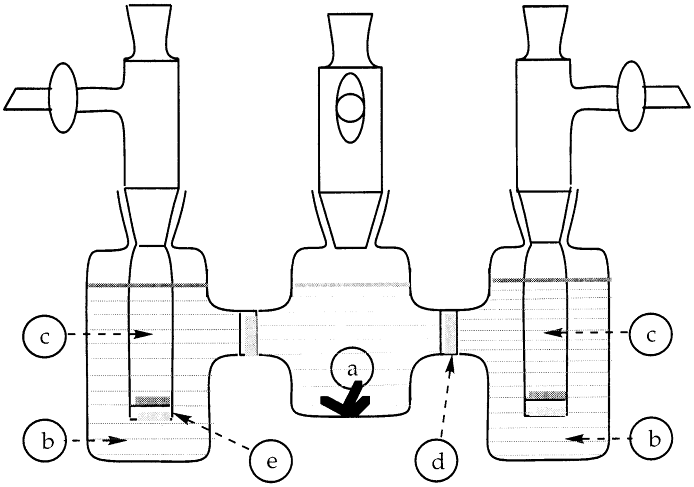


Fig. 2. Diffusion cell. (a) Solvent compartment; (b) saturated solutions of starting materials; (c) reservoirs containing saturated solutions and powder of starting materials; (d) low-porosity glass frits; (e) high-porosity glass frits.

$$n\mathrm{D} \rightarrow n\mathrm{D}^{+} + n\ \mathrm{e}^{-} \qquad (3)$$

and reacts with the $[\mathrm{M(dmit)_2}]^{-1}$ present in this compartment according to (Eq. (2)). Among the more than 40 $[\mathrm{D}][\mathrm{M(dmit)_2}]_y$ compounds, four superconducting phases have been characterized (Table 1).

All $\mathrm{M(dmit)_2}$ based superconductors reported so far are listed in Table 1, [21–28]. The year span ranges from 1986 up to date. They have been produced in four groups, those of Kobayashi, Tajima, Kato and mine. As for all molecule-based superconductors (excluding the fullerenes [16]) the critical superconducting transition is lower than 13 K. Most of the time, pressure is required for observing superconductivity. There is however one exception, the α-[EDT-TTF][$\mathrm{Ni(dmit)_2}$] phase which is superconducting at ambient pressure. It is interesting to note that the $\mathrm{M(dmit)_2}$ complex component can, alone, account for metal-like and superconducting behavior and doesn't require the presence of an organic donor.

As said above, in the previously mentioned organic donor based salts, such as those derived from BEDT-TTF-like molecules, the superconducting properties were related to the extended interactions between selenium or sulfur atoms on the periphery of the molecules. The $\mathrm{M(dmit)_2}$ systems possess ten sulfur atoms on their periphery, and indeed an extended network of S···S interactions is observed in the structure of all these compounds. Nonetheless, band structure calculations indicate that the $\mathrm{M(dmit)_2}$ systems should be considered at best as quasi-1-D systems [15].

## 3. Non-integral oxidation state in $\mathrm{M(dmit)_2}$ based salts

From the $x = 0.5$ stoichiometry in the $[\mathrm{C}]_{0.5}[\mathrm{M(dmit)_2}]$ phases, in which the associated countercation is a closed shell cation, such as for example $(\mathrm{Bu_4N})^{+}$, the partial formal oxidation state can be directly inferred, i.e. $[\mathrm{M(dmit)_2}]^{-0.5}$. The evaluation of the charge transfer is not as straightforward in the case of the donor–acceptor compounds where the associated countercation is an open shell cation radical, such as those derived from TTF-like donor molecules. In such donor–acceptor compounds, the formal charge of the $[\mathrm{M(dmit)_2}]^{n-}$ moiety cannot be inferred directly from the stoichiometry. Indeed, one of the important problems common to all classes of organic conductors is the determination of the oxidation state of molecules forming the conductive band, from which the filling of this band can be deduced. For TTF-derived organic conductors, comparing the molecular bond lengths obtained from X-ray structural determination provide some information about an approximate value of the charge transfer. However, this method is not very helpful for $\mathrm{M(dmit)_2}$-based compounds, since the bond length comparison in the $\mathrm{M(dmit)_2}$ units in different oxidation states show no clear trends within the limits of uncertainties in the measurements [12]. The charge transfer of such molecules can be determined with heavy-duty methods such as a combination of band structure calculation and diffuse X-ray scattering, as was made for (TTF)$[\mathrm{Ni(dmit)_2}]_2$ and α′-(TTF)$[\mathrm{Pd(dmit)_2}]_2$ [29,30]. Infrared and Raman spectroscopy offers a lighter option.

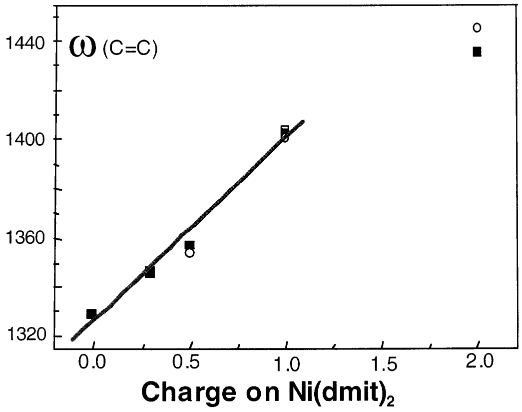


Fig. 3. Frequency shift of the C=C stretching mode as a function of the formal charge on the $[M(dmit)_2]^{n-}$ anion in $M(dmit)_2$ based compounds (■: M = Ni; ○: M = Pd).

The experimental Raman spectra of several $[Ni(dmit)_2]^-$ and $[Pd(dmit)_2]^-$ based compounds with known formal charge of the $[M(dmit)_2]^{n-}$ moiety have been recorded and assigned [31]. The C=C stretching ($A_g(1)$) mode, observed, for example, at 1328 $cm^{-1}$ in the Raman spectrum of neutral $Ni(dmit)_2$, is the most significant mode, because it couples very little with other modes. It has recently been found that the shift experimentally observed for these compounds linearly increases when the formal charge of the $[Ni(dmit)_2]^{n-}$ anion increases from 0 to 1 (Fig. 3). We have now at our disposal a simple method for evaluating the charge transfer in $[M(dmit)_2]^-$ based compounds to come [31].

## 4. Electrical behavior of $M(dmit)_2$ based NIOS salts and CDW instabilities

The physical properties of superconductors derived from $M(dmit)_2$ complexes as electron acceptors show some marked differences when compared with those of superconductors based on organic donors. This may be illustrated by the temperature/pressure phase diagram of α′-(TTF)$[Pd(dmit)_2]_2$ and (TTF)$[Ni(dmit)_2]_2$ [24,32], (Fig. 4). The purpose of such diagrams is to determine the domains of temperatures and pressures in which a system is in its various states, insulating, metallic or superconducting, the experimental points in Fig. 4 corresponding to the relevant critical temperature of the relevant transition at a given pressure.

From the features of the phase diagram of α′-(TTF)$[Pd(dmit)_2]_2$, and from diffuse X-ray scattering [33], it may be inferred that the insulating state is not induced by 1-D instabilities such as spin density wave (SDW) or spin Peierls (SP), which have often been observed in organic superconductors [10,11], but to charge density waves (CDW) [12]. The temperature/pressure phase diagram of (TTF)$[Ni(dmit)_2]_2$ is rather intricate. First, the superconducting critical temperature $T_c$ increases with pressure, this behavior had never been previously observed for any molecular superconductor. Second, at ambient pressure, this phase remains metallic down to 1.5 K. Finally, at very low temperature and in a narrow pressure range around 5.3 kbar, the superconducting ground state is 're-entrant' into the low-pressure insulating state. This peculiar behavior (as for the palladium analogue system) may again be explained by the occurrence of CDW instabilities connected to a unique multi-sheets Fermi surface based on both the HOMO and the LUMO bands [15,30,34] (and not only the HOMO band as in organic superconductors).

Thus, CDW instabilities seem to be crucial for determining the conducting behavior of the M(dmit)$_2$ based systems. A CDW instability is a periodical distortion of the crystal lattice inducing a spatial modulation of the charge density, and usually results from an important electron–phonon interaction, or in quasi 1-D systems from the formation of electron-hole pairs [35]. It may be indirectly detected by X-ray diffuse scattering [30,36]. It is more rare to experimentally observe such a CDW instability by temperature-dependent resistivity measurements, as was made in the case of the purely inorganic superconductor NbSe$_3$ [35].

Strong indication for such CDW instabilities in Ni(dmit)$_2$ based salts has been inferred from the observation of an anomalous resistivity maximum at ca. 40 K for (EDT-TTF)[Pd(dmit)$_2$] [37] and at ca. 14 K for α-(EDT-TTF)[Ni(dmit)$_2$] [38], (Fig. 5).

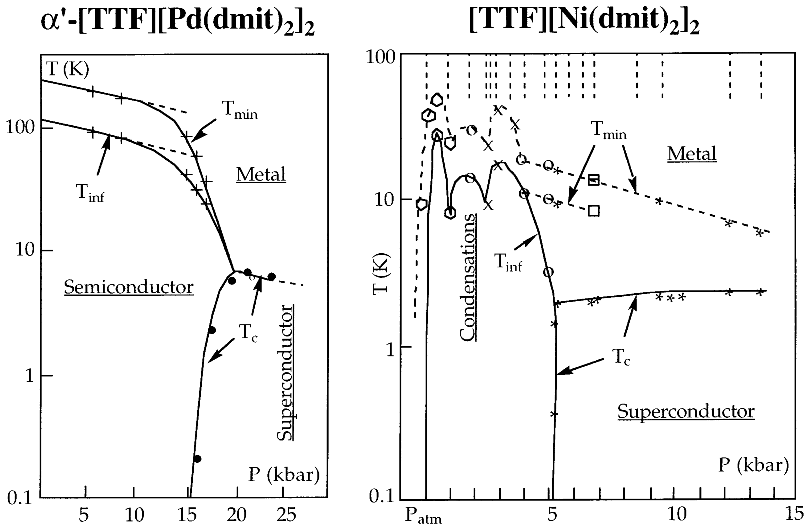


Fig. 4. Temperature/pressure phase diagram of α′-[TTF][Pd(dmit)$_2$]$_2$ and [TTF]{Ni(dmit)$_2$]$_2$ (redrawn after [24] and [32]). $T_{\min}$ is the temperature at which a minimum is observed in the resistivity versus temperature curve, indicating a gradual condensation of the carriers. $T_{\inf}$ is the temperature of the inflection point observed below $T_{\min}$ in the resistivity versus temperature curve. It is generally believed that the condensation of the carriers occurs gradually between $T_{\min}$ and $T_{\inf}$, and that $T_{\inf}$ actually is the temperature below which the metal-to-insulator transition is complete.

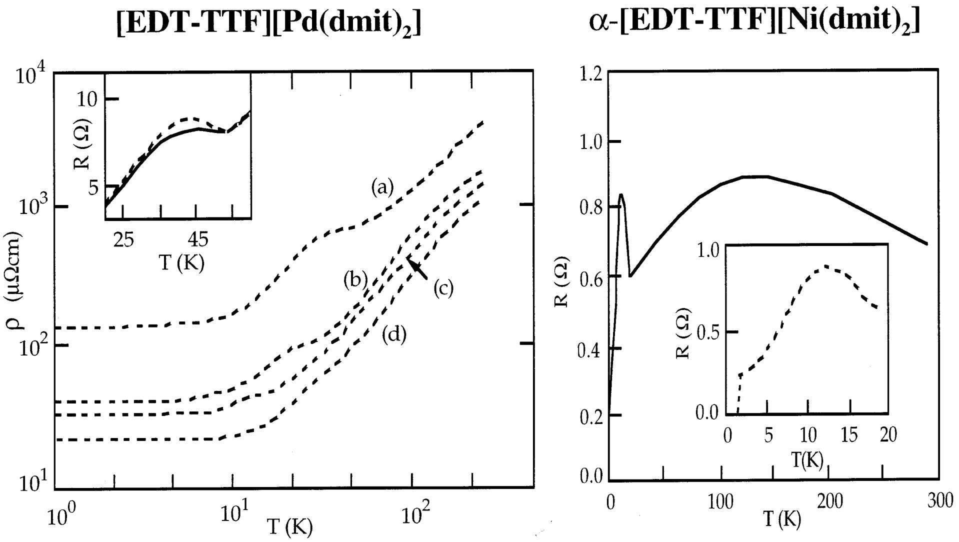


Fig. 5. Anomalous resistivity maximum at ca. 40 K for (EDT-TTF)[Pd(dmit)$_2$] (for an injected current $I$ of 150 μA at (a) ambient pressure, 2 kbar; (b) 5 kbar; (c) 10 kbar; (d) the insert shows the non-Ohmic behavior observed at ambient pressure for $I = 150$ (···) and 1.5 (—) μA), and at ca. 14 K for α-(EDT-TTF)[Ni(dmit)$_2$] (the inset shows the data below 20 K). Redrawn after [37] and [38].

The shift under pressure towards lower temperatures of the resistivity anomaly observed for (EDT-TTF)[Pd(dmit)$_2$], and the non-Ohmic behavior of this resistivity anomaly as a function of the injected current, are typical of the depinning of a CDW instability. Diffuse X-ray scattering experiments confirm the existence of a low temperature structural distortion, as evidenced by superlattice spots observed at 25 K and that vanish above ca. 45 K [39]. The existence of the CDW instability is further confirmed by the strong reduction (50% of the density of states) of the magnetic spin susceptibility observed at ca. 45 K, which indicates that the gap opening is only partial. Finally, these experimental data have been rationalized by tight-binding band structure calculations which show that, only the donor EDT-TTF stacks are affected by the CDW-Peierls transition [39].

The same analysis has been extended to the α-(EDT-TTF)[Ni(dmit)$_2$] ambient pressure superconducting phase and suggests that the resistivity anomaly observed at ca. 14 K in this compound is likewise due to a CDW instability, in agreement with magnetoresistance data [38,40]. However, the absence in the diffuse X-ray scattering data of superlattice spots led to suggest that the 14 K resistivity anomaly could as well result from a partial nesting of the Fermi surface due to a SDW condensation [41].

## 5. The impact of ‘dimerization’ in $M(dmit)_2$ systems on band structure calculation results

Band structure calculations have been carried out for a number of $M(dmit)_2$ based systems, and these studies emphasized the crucial role of the ‘dimerization’ within the $M(dmit)_2$ stacks [15]. Dimerization here means that the interplanar distance between the $M(dmit)_2$ units along a stack is not constant. In these compounds, depending on the strength of the transfer integrals with respect to the HOMO-LUMO splitting, the partially filled band can originate either from the LUMO for weakly dimerized systems, or from the HOMO for the strongly dimerized systems [34](Fig. 6).

Either situation is found in the band structure of $(Me_4N)_{0.5}[Ni(dmit)_2]$ and $Cs_{0.5}[Pd(dmit)_2]$. In $(Me_4N)_{0.5}[Ni(dmit)_2]$ which is weakly dimerized, the partially filled band is mainly built from the LUMO, as could be intuitively expected. By contrast, in $Cs_{0.5}[Pd(dmit)_2]$ which is more strongly dimerized, the partially filled band is almost exclusively built from the HOMO [15,34]. These different situations have a strong impact on the properties of the concerned compounds. For example, the $[Me_2Et_2N]_{0.5}[Pd(dmit)_2]$ phase undergoes a superconducting transition at 4 K and 2.4 kbar, and a peculiar restoration of an insulating state at pressures higher than 7 kbar [26]. The structure of $[Me_2Et_2N]_{0.5}[Pd(dmit)_2]$ consists of strongly dimerized $[Pd(dmit)_2]_2$ stacked anions. As discussed above, the conduction band of such a strongly dimerized system originates, at low pressure, mainly from the HOMO and tight-binding band structure calculations indicate a 2-D metallic Fermi surface. High pressure may induce a more regular stacking arrangement and, consequently, a 2-D → 1-D dimensionality crossover, possibly resulting in a 1-D instability which could account for the insulating state observed at high pressures.

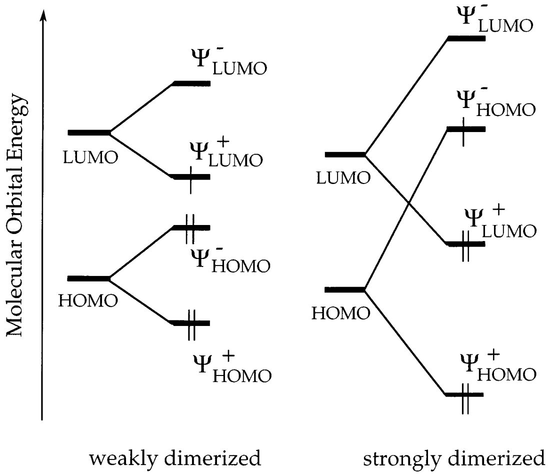


Fig. 6. HOMO and LUMO levels for weakly and strongly dimerized $M(dmit)_2$ systems (from [34]).

## 6. Other applications of $M(dmit)_2$ systems and interplay of conductivity, magnetism and nonlinear optics

The $M(dmit)_2$ based systems, and more generally, the bis-dithiolate metal complexes have not been studied only for their conducting behavior in the solid state. Among other applications, are the possibility of producing Langmuir-Blodgett (LB) films, materials exhibiting nonlinear optical (NLO) properties or unconventional magnetic properties.

For example, Bryce et al. have studied the possible use of $(Bu_4N)[Nidmit)_2]$ at the air–water interface in the making of conducting LB films. These films were built up on a variety of substrate from the floating layer containing tricosanoic acid [42]. Decent room temperature (r.t.) conductivities (ca. 10–2 S cm$^{-1}$, with $E_a$ ca. 0.1 eV) have been achieved by post deposition electrochemical or iodine doping.

As for NLO properties, Drexhage et al., in an earlier patent [43], pointed out that metal bis-dithiolate metal complexes may be well suited for Q-switching lasers (such as Nd-Yag lasers, operating at 1064 nm). More recently, third order optical nonlinearity have been observed for a range of nickel bis-dithiolate metal complexes, and possible utilization in the fabrication of all-optical signal processing devices have been predicted [44,45]. One may wonder whether coupling conducting and NLO properties are not impossible challenges, as high conductivity is associated with lack of transparency. It should be recalled that semiconductors possess a transparency in the near-infrared region sufficient for optical purposes. Moreover, modern photonics will require ultra-short (sub-pico) pulses of light, and thus the use of micron-thick materials for avoiding velocity dispersion. Nevertheless, one should gracefully admit that these technological developments are only in their infancy.

The parallel quest towards molecule-based ferromagnets has prompted several authors active in this field to evaluate the possible use of bis-dithiolate metal complexes in making such magnetic materials. In fact, the bis-dithiolate metal anions, $[M(bdt)_2]^-$ (bdt = benzenedithiolato) seems to meet the requirements proposed by McConnell for the stabilization of ferromagnetism in linear chain alternating...$(D^+)(A^-)(D^+)(A^-)(D^+)(A^-)$...compounds by virtual charge transfer between donor and acceptor, $(D^+)\leftrightarrow[M(bdt)_2]^-$ [46]. When using bisdithiolate metal anions with M = Ni, Pd, Pt, Fe and dithiolate = dmit, dmio (2-oxo-1,3-dithiole-4,5-dithiolato), mnt (maleonitriledithiolato), bdt, trifluoromethylethylenedithiolato, in combination with a metallocenium such as $[(Me_5C_5)_2M']^-$ with M′ = Fe, Mn, ferromagnetic interaction was observed down to low temperatures, but no magnetic ordering in most cases [47]. However, metamagnetic behavior was observed in a few cases [48].

Up to now, this short, supposedly tutorial review concentrated on metal bis-dithiolato compounds exhibiting only one unconventional physical behavior (and this is difficult enough to achieve!), either conductivity and superconductivity, or NLO, or magnetic properties. An even higher challenge could be set, which may be designated by the word ‘interplay’, and would consist of designing molecule-based materials in which two, or more, of such properties would co-exist, or even more ambitiously (and useful for producing devices), would be coupled in some way.

For example, among several bis-dithiolate metal complexes which have been used for the formation of semiconducting salts with TTF or TTT (tetrathiotetracene),[49], several members in this series of the type [TTF][$MS_4C_4(CF_3)_4$] (M = Cu, Au, X = S, Se) exhibit quasi 1-D Heisenberg antiferromagnetic spin behavior above 12 K, but undergo a unique second-order transition at lower temperatures ( < 12 K for M = Cu, X = S; < 2 K for M = Cu, X = S; < 6 K for M = Cu, X = Se) to a diamagnetic state which has been characterized as a spin-Peierls transition [50].

The α-(perylene)$_2$[M(mnt)$_2$] (mnt = maleonitriledithiolato) compounds were one of the first systems to exhibit, at least, a coexistence of conducting and magnetic properties, and possibly an interplay of both properties [51]. In these compounds, chains of perylene cations provide highly anisotropic metallic properties whereas segregated [M(mnt)$_2$]$^{z-}$ chains with appropriate metals (M = Ni, Pd, Pt, Fe) supply localized magnetic moments. Although these two chains are prone to exhibit the instabilities typical of 1-D conducting systems (Peierls, for the perylene chains) and magnetic (spin-Peierls, for the [M(mnt)$_2$]$^{z-}$ chains), π conduction electrons in perylene chains and magnetic moments of the [M(mnt)$_2$]$^{z-}$ chains coexist to low temperatures (down to 8 K for α-(perylene)$_2$[Pt(mnt)$_2$]. Moreover, both instabilities occur at the same temperature. What is the interaction mechanism between the chains and which instability, Peierls or spin-Peierls, provides the driving force for the transition, were, and still are pending questions. Let me mention, in passing, that the recently reported (DT-TTF)$_2$[M(mnt)$_2$] compound exhibits, in addition to a high conductivity (8 S cm$^{-1}$ at r.t.), a spin-ladder behavior [52]. The static magnetic susceptibility of this compound shows an activated behavior above 70 K and a Curie–Weiss behavior at higher temperatures, which are typical of a system having localized spins (on [(DT-TTF)$_2$]$^+$ dimers) with strong antiferromagnetic interactions, and which displays a spin gap.

One similar strategy that we use in our group consists in preparing M(dmit)$_2$ salts with a paramagnetic cations. For example, in [$(Me_5C_5)_2Mn$][Ni(dmit)$_2$] the [$(Me_5C_5)_2Mn$]$^+$ contains two unpaired electrons ($S = 1$, d4, 16 electrons). The [Ni(dmit)$_2$]$^-$ anionic unit is also magnetic with $S = 1/2$. Static magnetic susceptibility measurements show that the product χT is almost constant from r.t. to 5 K. Below 5 K, χT increases sharply [53] (Fig. 7a). This is due to a ferromagnetic interaction in the compound, as confirmed by field cooled magnetization, remnant magnetization and zero field cooled magnetization measurements at 2 K (Fig. 7b). Thus, the ($Cp_2^*Mn$)[Ni(dmit)$_2$] is the first ferromagnet based on Ni(dmit)$_2$ systems.

This previous complex has been electro-oxidized and a conducting powder has been obtained (0.3 S cm$^{-1}$ at r.t.), indicating that a non-integral oxidation state complex has been obtained.

Another interplay which can be envisioned is that of conductivity and nonlinear optics (NLO). Again, a simple strategy may consist in combining in the same molecular unit a component affording conducting properties, M(dmit)$_2$ systems for example, and a component known for exhibiting NLO properties. Salts of the (DAMS)$^+$ cation (4-[2-(4,4-dimethylaminophenyl)ethenyl]-1-methylpyridinium;

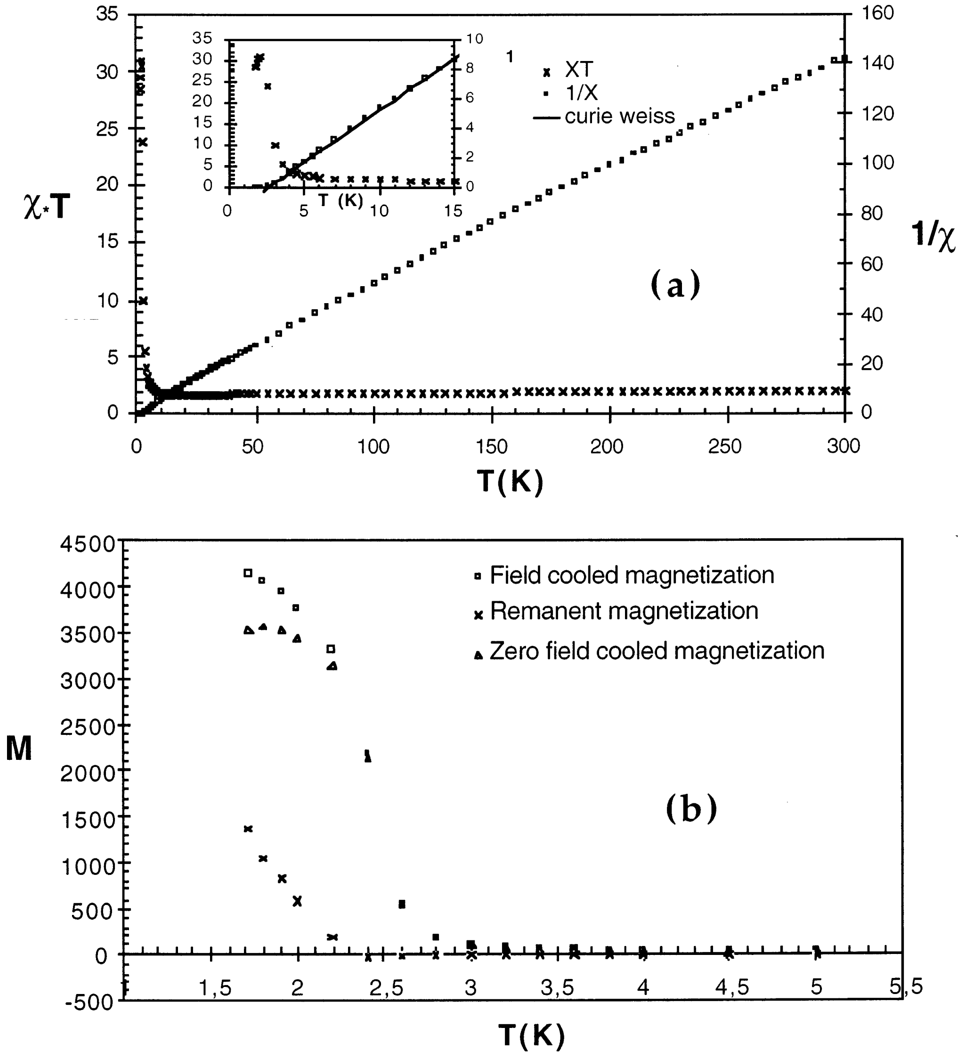
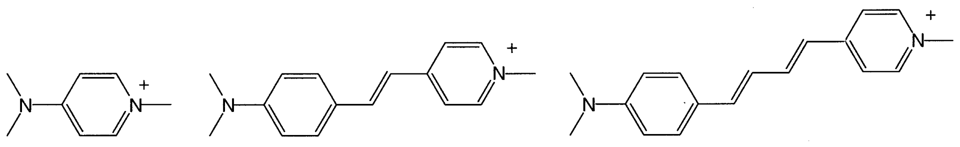


Fig. 7. (a) Static magnetic susceptibility ($\chi*T$ and$1/\chi$), and (b) magnetization (M), as a function of temperature.

Scheme 5) are among the most efficient chromophores for second harmonic generation [54]. Thus, 1:1 salts of $(DAMS)^+$ and similar systems, such as $(DAMP)^+$ (4-dimethylamino-1-methylpyridinium) and $(DABMP)^+$ (4-[4-(4-dimethylaminophenyl)-1,3-butadienyl]-1-methylpyridinium), combined with the $[Ni(dmit)_2]^-$ anion were prepared by metathesis reaction between the appropriate chromophore salt and $(Bu_4N)[M(dmit)_2]$ [55].

For example, the structure of $(DAMP)[M(dmit)_2]$ is monoclinic, with space group $P2_1/c$, and thus centrosymmetric (Fig. 8). The asymmetric unit contains two



**DAMP$^+$** **DAMS$^+$** **DABMP$^+$**

Scheme 5.

$[Ni(dmit)_2]^-$ and two $(DAMP)^+$ entities. The structure consists of layers of $[Ni(dmit)_2]^-$ anions separated by layers of $(DAMP)^+$ cations. Within a layer, a number of S···S short distances extending in two directions are observed between the $[Ni(dmit)_2]^-$ units. This may explain why the conductivity of this phase is rather high ($1.3 \times 10^{-2}$ S cm$^{-1}$, $E_a = 0.05$ eV) for such a 1:1 $Ni(dmit)_2$-based salt.

Unfortunately (as far as NLO properties are concerned), the structure is centrosymmetric, as well as those of the $Ni(dmit)_2$ salts with the $(DAMS)^+$ and $(DABMP)^+$ cations (in fact, most, i.e. 98% of compounds derived from $M(dmit)_2$ have centrosymmetric structures [12a]. Thus, as it is known that second order NLO properties require non-centrosymmetry [56], the $(DAMP)[M(dmit)_2]$ compound shows no efficiency. Along this line still, the structure of $(DAMP)[M(dmit)_2]$ shows an interesting feature concerning the arrangement of the $(DAMP)^+$ cations (Fig. 8b): within their own layer, the $(DAMP)^+$ cations are arranged in a non-centrosymmetric fashion. Moreover, the use of chiral DAMS-like derivative may offer a path circumventing the difficulty associated to the ubiquitous non-centrosymmetrical structural arrangement of $M(dmit)_2$-derived salts.

## 7. Conclusion

Systems based on metal bis-dithiolato complexes, and especially $M(dmit)_2$, are the sole molecular transition metal compounds exhibiting highly conducting or superconducting properties. The electrical behavior of these systems is often related to charge density wave instabilities. This behavior is determined by the degree of 'dimerization' in the structure. Bis-dithiolate metal complexes may be used as 'building blocks' in the preparation of hybrid systems exhibiting a co-existence or an interplay of several properties (conducting, NLO, magnetic,...).

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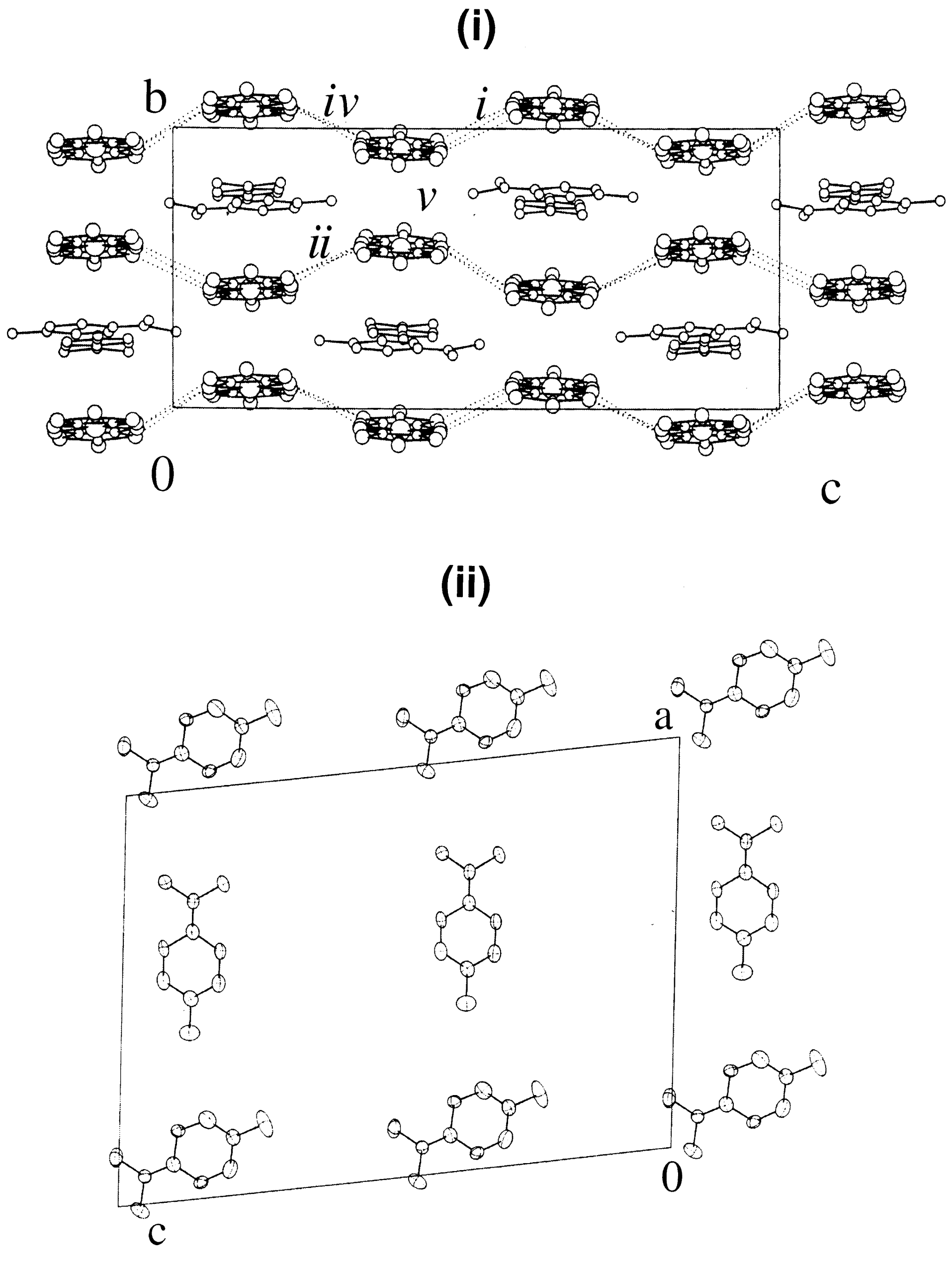

Fig. 8. Structure of (DMAP)[Ni(dmit)$_2$]. (i) Projection of the Ni(dmit)$_2$ layers onto the *bc* plane. (ii) Projection of the DAMP$^+$ layers onto the *ac* plane. Redrawn after [55].

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