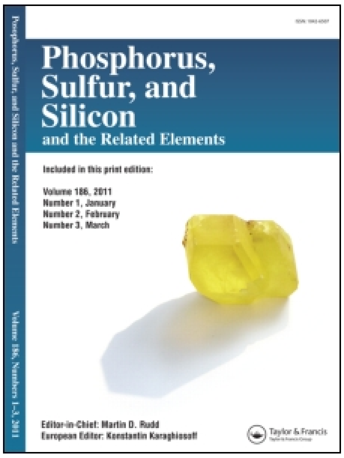

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Molecular Conductors Based on Complex Metal Anions

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MOLECULAR CONDUCTORS BASED ON COMPLEX METAL ANIONS

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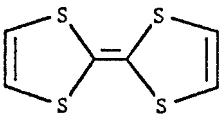
ABSTRACT

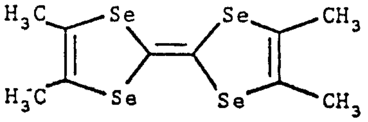
The preparation, structure and electrical conductivity of metal complexes of mnt and dmit with Group 1 cations are described.

INTRODUCTION

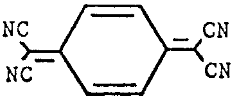
During the last twenty years there has been intense activity to synthesise and study molecular metals and superconductors. The first molecular metals were based on the platinum atom chain compounds containing cyanide or oxalate.[1] The most widely studied molecular metals and superconductors have been based on organic donor molecules such as TTF, TMTSF, or BEDT-TTF. These compounds contain sulphur or selenium heterotoms within a highly delocalised planar molecule. TTF.TCNQ was the first organic metal to be studied in detail. The selenium-containing donor, TMTSF, yielded the first organic molecular superconductor, $(TMTSF)_2PF_6$(Tc = 0.9K at 6.5K bar) and the first ambient pressure molecular superconductor $(TMTSF)_2ClO_4$(Tc = 1.4K).[2] BEDT-TTF, first synthesised in 1978[3] is the most versatile of the organic donors in the preparation of molecular metals and superconductors and currently there are about 18 known molecular superconductors based on this organic donor. A characteristic of the structures of molecular metals and superconductors containing these organic donors is the existence of S...S or Se...Se inter-molecular interactions at distances less than the sum of the Van der Waals radii. It is through these interactions that the phase transitions which convert molecular metals into semiconductors are suppressed, and hence the metallic state stabilised at low temperatures. At the present time $[\mathrm{BEDT\text{-}TTF}]_2[\mathrm{Cu(N(CN)_2)Cl}]$ holds the record for a molecular superconductor with a transition temperature of almost 13K.[4] There are now over 30 known molecular superconductors based on organic donors heterocyclic containing either sulphur or selenium atoms.



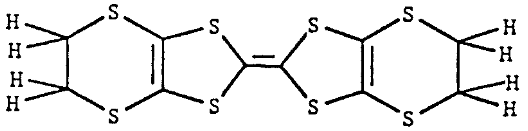
TTF



TMTSF

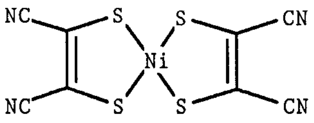


TCNQ

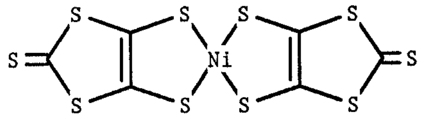


BEDT-TTF

In parallel to the work on molecular metals and superconductors based on the organic donor molecules described above, there has been a related investigation of metal complexes of sulphur-donor ligands. These ligands, such as 1,2-dicyanoethylene-1,2-dithiol(mnt) and 4,5-dimercapto-1,3-dithiol-2-thione(dmit) bear strong structural similarities to fragments of the organic donors described above. Thus the $[\mathrm{M(mnt)_2}]^{x-}$ anion has similarities to the TTF cation and the $[\mathrm{M(dmit)_2}]^{x-}$ anion is similar to the BEDT-TTF cation.



$[\mathrm{Ni(mnt)_2}]^{x-}$



$[\mathrm{Ni(dmit)}]^{x-}$

METAL COMPLEXES OF 1,2-DICYANOETHYLENE-1,2-DITHIOL(mnt)

As discussed above there is a marked molecular structural similarity between TTF and metal complexes of mnt.

Transition metal complexes of 1,2-dicyanoethylene-1,2-dithiol (maleonitrile, mnt), have received special study since this ligand can stabilise transition metals in a variety of oxidation states and the high electron affinity of the terminal cyanide groups aids the delocalisation of charge within the complex, thus reducing potential coulombic repulsions. In an attempt to maximise interactions between the metal dithiolene anions Underhill and Ahmad studied the cation deficient compound $(H_3O)_{0.33}Li_{0.8}[Pt(S_2C_2(CN)_2)_2]1.67H_2O(LiPt(mnt))$.[5] X-ray studies show that the room temperature structure (Figure 1) of LiPt(mnt) consists of equidistant stacks of nearly eclipsed $[(Pt(mnt)_2]$ anions along the c-axis, with c = 3.639 A.[6] The unit cell is triclinic and the stacks form sheets along b separated along a by Li^+ and H_2O (Figure 1).

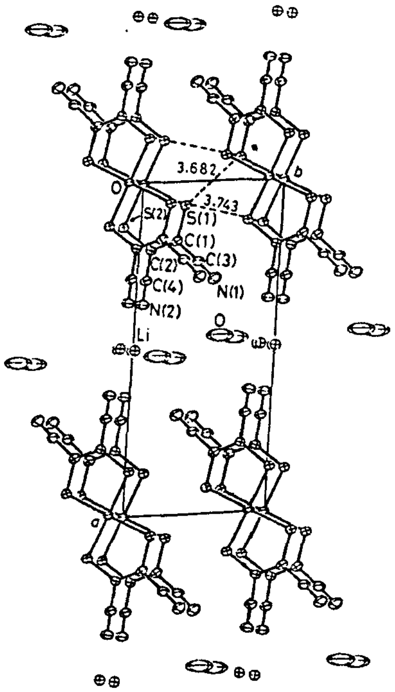


FIGURE 1 The c axis projection of the crystal structure LiPtmnt

There are short sulphur contacts between the chains within the sheets as well as within the chain, suggesting a relatively two dimensional network. Although the compound is cation deficient, the long Pt-Pt interchain separation shows that the bonding within the chain cannot be of the simple metal orbital overlap type. The high room temperature conductivity of ~ 100 Scm^{-1} in the stack direction must therefore result from interactions between the anions as molecular species in the chain direction. The temperature dependence of the electrical conductivity along the stack direction (σ") for freshly prepared crystals slowly increases with decreasing temperature with σ" passing through a maximum at about 250K (Figure 2).

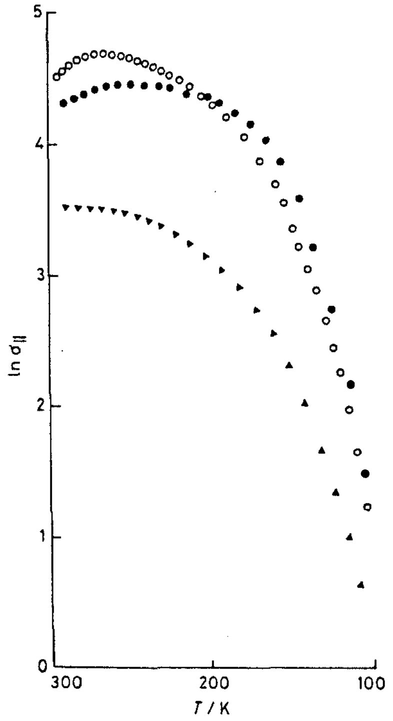


FIGURE 2 Variation of conductivity with temperature for crystals of LiPt(mnt) (O) freshly cropped; (●) crystals stored at 75% relative humidity; (▼) stored at ambient humidity for 14 d.[5]

The conductivity falls to its room temperature value at about 200K and then falls rapidly with decreasing temperature. Below 100K the behaviour is that of a semiconductor with an activation energy of about 34 meV. The changeover in the conductivity behaviour from that of a metal to that of a semiconductor with decreasing temperature is common in this class of compound. It is a result of the pseudo nature of the interactions which lead to the metallic properties. From the structure of the compound the principal interactions which give rise to intermolecular overlap are the intermolecular sulphur-sulphur contacts in the stack direction. There are also weaker contacts between molecules in adjacent stacks along b. The metal to semiconductor transition is a manifestation of the Peierls instability of a one-dimensional metal.[7]

One-dimensional metals are inherently unstable to a periodic lattice distortion which has the effect of splitting the partially filled band of a one-dimension metal to give filled and empty bands characteristic of a semiconductor. The occurrence of the Peierls distortion in this compound has been confirmed by crystallographic studies which have shown a superstructure below T_c = 215K which is preceeded by a one-dimensional diffuse X-ray scattering typical of a Peierls transition. The position of the diffuse line along c indicates that the extent of band filling is 0.41 or 0.59. Studies have shown that the thermopower above T_c is approximately constant and positive implying hole characteristics for the carriers in the metallic region and therefore, the extent of band filling is 0.59. Below T_c the thermopower reflects the intrinsic properties of the charge density wave semiconductor.[8]

An extensive study of $[M(mnt)_2]$(M = Ni,Pd,Pt, etc.) complexes failed to produce other examples of molecular metals based on this metal complex anion under ambient conditions.

Some salts such as $Cs_{0.82}[Pd(mnt)_2].0.5H_2O$, although exhibiting a relatively high electrical conductivity (5 Scm^{-1}) at room temperature, exhibit the temperature dependence of conductivity of a semiconductor.

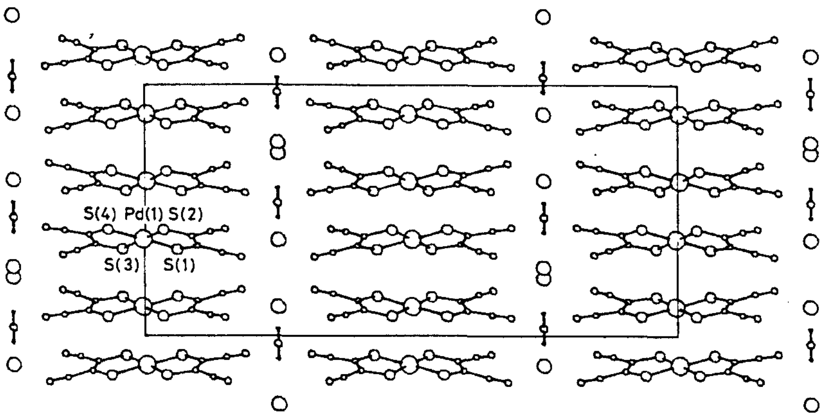


FIGURE 3 A view of the crystal structure of $Cs_{0.82}[Pd(S_2C_2(CN)_2)_2]_{0.5}H_2O$ down the a-axis.

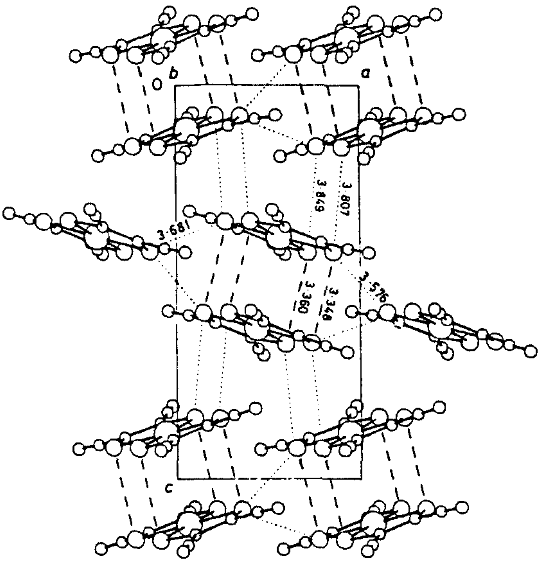


FIGURE 4 A view along the b-axis of $Cs_{0.82}[Pd(S_2C_2(CN)_2)_2]0.5H_2O$ showing the structure of the anion sheet.

However, under increasing pressure the value of the room temperature conductivity rises and the temperature dependence of the conductivity becomes that of a metal, i.e. rising with decreasing temperature. At relatively low pressures there is still a metal to semiconductor transition at low temperatures, but at the highest pressure studied, 21.3kbar, the compound behaved as a metal down to 1.3K. (See Figure 3)[9]

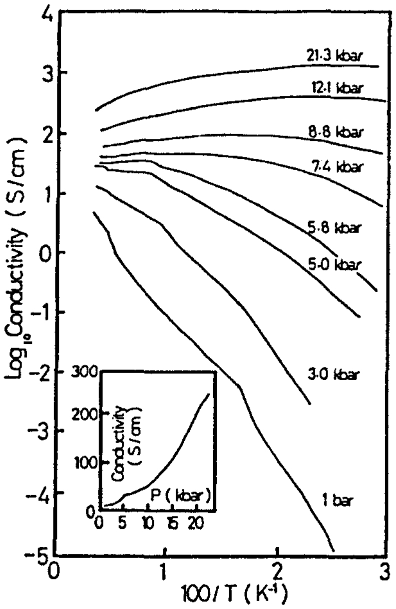


FIGURE 5 Temperature dependence of the conductivity of $Cs_{0.82}[Pd(S_2C_2(CN)_2)_2]0.5H_2O$ at various pressures. Insert shows the pressure dependence of the conductivity at room temperature.

METAL COMPLEXES OF 4,5-DIMERCAPTO-1,3-DITHIOLE-2,THIONE(dmit)

There is considerable structural similarity between the organic donor BEDT-TTF and the metal complexes of dmit. In order to suppress the Peierls instability in complexes, it is necessary to increase the inter-stack interactions. The ligand dmit, containing five peripheral sulphur atoms is clearly an improvement on the simple mnt dithiolene ligand. Since its discovery in 1975 by Steimecke and co-workers[10], large numbers of metal complexes of this ligand have been prepared, studied and recently reviewed.[11]

Most of the studies have been concerned with the square co-planar complex anions containing the metals Ni(II), Pd(II), Pt(II) and Au(III). In these complexes, the HOMO and LUMO are constructed from a combination of the central metal d orbitals and ligand π-orbitals. The metal complexes can exist as the di-anion species in which both the HOMO and LUMO containing a pair of electrons, as a mono-anion in which the LUMO contains a single electron and the neutral metal complex in which the LUMO is empty. It is a characteristic of metal complexes of sulphur-donor ligands of this type that they exhibit reversible redox activity in solution. In addition, the neutral metal complex and the mono-anionic complex exhibit intense near infra red absorption arising from the HOMO to LUMO transition.

In the solid state the metal complexes commonly adopt a stack structure involving strong S...S interactions between adjacent molecules within the stack and between molecules in adjacent stacks. These interactions lead to the formation of delocalised bands within the structure and give rise to the electrical conduction properties observed for this class of compound.

The $M(dmit)_2$ complexes can be conveniently divided into those with "open-shell" organic cations such as TTF or BEDT-TTF, those with "closed-shell" organic cations, such as NMe_4^+ and those with inorganic cations. We have made a particular study of salts with inorganic cations and those of group 1 and group 2 cations in particular. Our choice of these cations was based on the assumption that the smaller the counter-cation the greater will be the interactions between the $M(dmit)_2$ anions and hence the greater the inter-molecular interactions thus facilitating the stabilisation of the metallic or superconducting state.

[Ni(dmit)$_2$] SALTS WITH INORGANIC CATIONS

Early work suggested that compounds with $M_x[Ni(dmit)_2]$ stoichiometry (where M is Li or Na, $0 < x < 0.5$) were semiconducting.[12] Recently we have carried out more detailed work to show that well defined salts, M[Ni(dmit)$_2$]$_2$ (M = Li, Na, or K), can be obtained by electrocrystallisation of acetonitrile solutions of (n-Bu$_4$N)$_2$[Ni(dmit)$_2$] in the presence of a large excess of Group 1 metal cations.[13,14]

(a) Li[Ni(dmit)$_2$]$_2$.2CH$_3$CN

Electrochemical synthesis generated poorly formed plate-like crystals with Li[Ni(dmit)$_2$]$_2$.2CH$_3$CN stoichiometry. Variable temperature conductivity studies on compressed pellets showed the compound to be a well-behaved semiconductor in the temperature range 300-40K and with an activation energy of ~0.02 eV and a room temperature conductivity of ~0.6 Scm^{-1}.

(b) Na[Ni(dmit)$_2$]$_2$

Na[Ni(dmit)$_2$]$_2$ was obtained as shiny black, well-formed needles. The crystals were of a quality just below that required for a complete X-ray crystal structure determination. However, from X-ray oscillation photographs the system appears to be essentially one-dimensional with a regular spacing of 3.79 Å.
The room temperature conductivities of three crystals were determined and were found to lie between 1 and 100 Scm^{-1}. All the crystals examined showed simple metallic behaviour down to at least 2K and one crystal showed metal-like conductivity down to 25mK. The conductivity was studied under pressures of up to 6 kbar and whilst resistivity shows the expected decrease with increasing pressure, there was no evidence for superconductivity at temperatures down to 2K (see Figure 6).

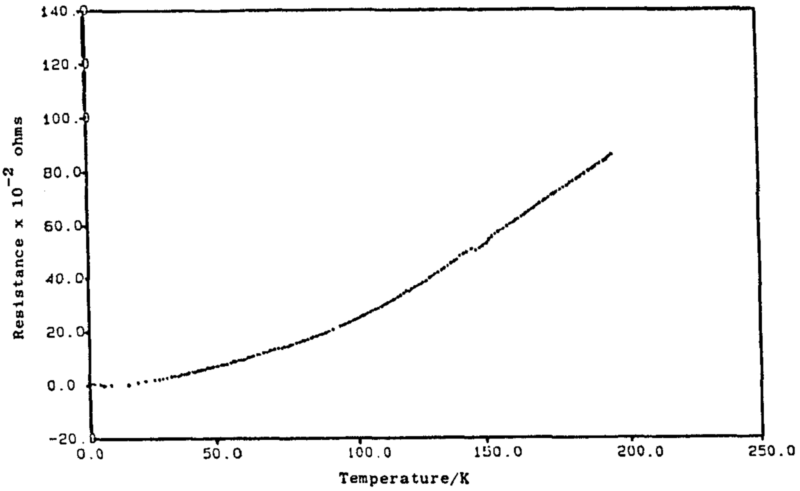


FIGURE 6 The temperature dependence of the conductivity of a crystal of $Na[Ni(dmit)_2]_2$.

The thermopower is negative with a value of -15μV/K at 300K. It falls on cooling towards zero, with no suggestion of a sign change above 30K. The sign of the thermopower indicates electrons as the charge carriers and the value is typical of that of a simple metal. The magnetic susceptibility of the salt as a function of temperature was also measured.

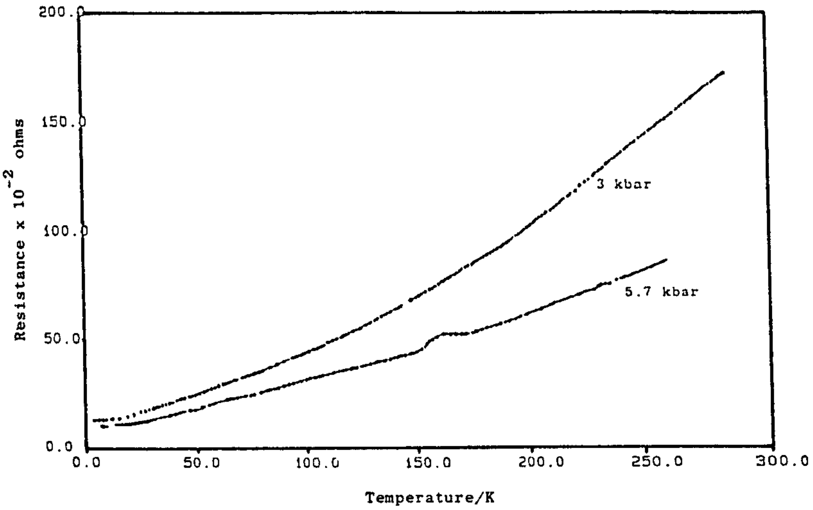


FIGURE 7 The temperature dependence of the conductivity of $Na[Ni(dmit)_2]_2$ under pressure.

The value of the temperature independent term after subtraction of the effect of magnetic impurities is consistent with contributions from both core diamagnetic and Pauli paramagnetic terms.

(c) $K_{0.4}[Ni(dmit)_2]$

$K_{0.4}[Ni(dmit)_2]$ was obtained as black, poorly-formed plates by electrocrystallisation. As with the previous example, the crystals were of a quality insufficient for a full crystal structure determination. Initial X-ray oscillation photographs, indicate that the structure is similar to the salt $Na[Ni(dmit)_2]_2$ in that it appears to be a regular stacked structure of interplanar distance of approximately 3.72Å.

The electrical conductivity of the salt was examined by measuring along the longest axis of the crystal. The room temperature conductivity of several crystals was found to lie between 10 and 230 Scm^{-1}.[15] The temperature dependence of the conductivity was investigated for several samples, but gave inconsistent results. Some crystals showed a steady increase in conductivity down to 20K. Others, after the conductivity increased with decreasing temperature down to between 160 and 120K, showed a small decrease in conductivity below this temperature. The fall in conductivity, however, was small compared with that observed for compounds known to undergo a metal to semiconductor transition. Other crystals showed a clear transition to semiconductor behaviour at ~150 - 100K. For some crystals, abrupt falls in conductivity were observed at various temperatures and this type of behaviour has been ascribed to the development of micro-cracks in the sample.

Although the precise electrical behaviour of the compound at ambient pressure has not been fully determined, the temperature dependence of the conductivity under increased pressure has been studied. At ambient pressure, the crystal shows metal-like electrical conductivity down to approximately 140K, at which point a very broad transition to a semiconducting state is seen, characterised by a marked rise in the electrical resistivity. Applying a pressure of

3.5 kbar serves to approximately halve the room temperature conductivity. With decreasing temperature, the crystal again maintains metal-like conductivity down to 140K, at which point the onset of a very broad transition is apparent. Whilst the increased pressure serves to drop the overal resistivity, it does not serve to maintain the metallic state below 140K.

Variable temperature magnetic susceptibility measurements have been carried out on $K_{0.4}[Ni(dmit)_2]$. In a similar way to $Na[Ni(dmit)_2]_2$, the graph of χ vs temperature follows a Curie-Weiss law. Again, the Pauli paramagnetic, temperature-independent contribuition to the graph, resulting from the spin of the conduction electrons, cannot be seen at low temperature due to the large Curie-Weiss type behaviour. At the metal to semiconductor transition temperature, the metallic contribution to the susceptibility should fall to zero, thus enabling the transition temperature to be more accurately determined. Unfortunately, no sharp discontinuities could be observed, presumably because the susceptibility associated with the large number of crystal defects is masking any such effect.

(d) Salts with Rubidium and Caesium

As discussed above, it proved relatively easy to prepare salts of $[Ni(dmit)_2]$ with Li,Na and K cations. Attempts to grow crystals of either the rubidium or the caesium salts under similar conditions, were not successful. The majority of the experiments failed to produce any crystals on the anode or grew the tetrabutylammonium monoanionic salt despite the presence of a large excess of the Group 1 metal salt.

DISCUSSION

The salts of $[M(dmit)_2]$ anions have generally proved much more difficult to prepare than the corresponding salts of the $[M(mnt)_2]$ anions. This is particularly true of the group I metal salts and consequently, the studies undertaken have been far less extensive. In general, electrocrystallisation experiments performed with the $[Ni(mnt)_2]$ anion grew the monoanionic salt with the particular group

1 metal[16] $N[M(mnt)_2]$ whereas the "dmit" system has a marked tendency to grow a partially oxidised system of the type $N[M(dmit)_2]_2$. The vast majority of room temperature molecular metals based on metal complex anions exhibit a metal to semiconductor transition at temperatures above 20K. The behaviour of $Na[Ni(dmit)_2]_2$ is most unusual in retaining its metallic properties down to such a low temperature as 25 mK. Unfortunately, a full crystal structure for the compound cannot be determined as yet and so the reason for this unusual behaviour cannot be ascertained. However, the preliminary evidence for an equidistant stack structure may be significant. Superconductivity in metal complexes has only been observed at low temperatures under high pressure. Up to the present time, the conduction studies have been restricted to pressures up to 6 kbar and no evidence of superconductivity has been obtained. Furthermore, these studies give no indication that superconductivity could be expected at high pressures. Nevertheless, the synthesis of a material of this type which retains its metallic properties down to such low temperatures is an important development in the field of molecular metals and superconductors and further stueids of $M(dmit)_2$ salts are in progress.

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