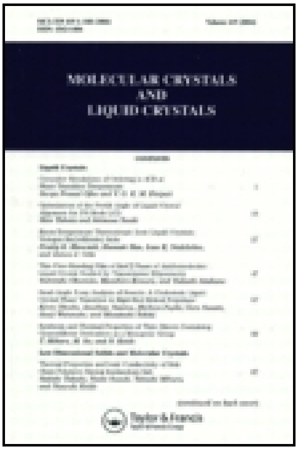

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Molecular Compounds Exhibiting Coupled Conducting and Magnetic Properties and Based on $(cation)_n[M(dmit)]_2$ and $(BETS)_2(anion)$ Salts

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MOLECULAR COMPOUNDS EXHIBITING COUPLED CONDUCTING AND MAGNETIC PROPERTIES AND BASED ON $(cation)_n[M(dmit)]_2$ AND $(BETS)_2(anion)$ SALTS

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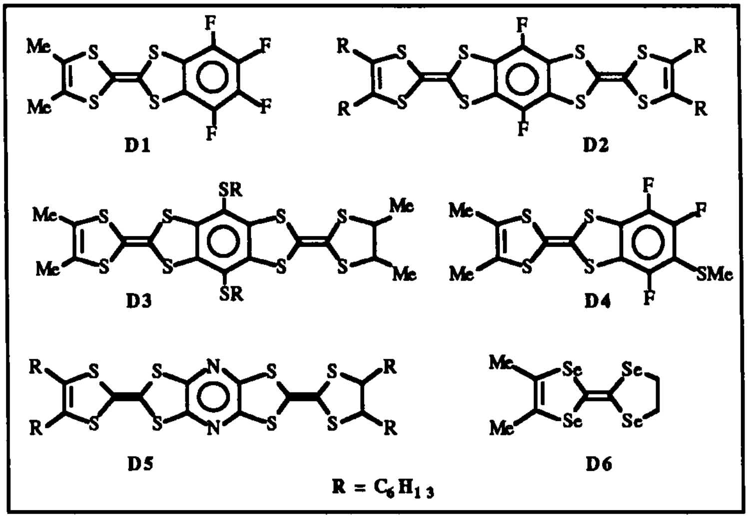
Abstract. A systematic study has been carried out on a range of metal complexes of the type $(cation)_n[M(dmit)_2]$ (cation = NH_yR_{4-y}; y = 1 or 2; n = x, 1, 2; R = ethyl, propyl or butyl, or cation = organic radical cations containing one or two TTF moieties; M = Ni or Pd and dmit = 2-thioxo-1,3-dithiole-4,5-dithiolato). The synthesis of these complexes, the crystal structure of $(NHBu_3)_2[Ni(dmit)_2]$ and neutral $[Ni(dmit)_2]$, their solution redox behaviour and the solid state conductivities of the non-integer oxidation state compounds obtained by electrocrystallization techniques are presented. Synthesis, structure and properties of new compounds of the family of $(BETS)_2(anion)$ compounds with $(Cu_xCl_y)^{n-}$ and $[(FeCl_4)_{1-x}(GaCl_4)_x]^-$ anions are described.

INTRODUCTION

Over the last two decades, a great deal of interest has been shown in metal complexes derived from the dmit ligand as several of the derived non-integer oxidation state (NIOS) complexes containing alkali metal cations, closed shell cations and open shell organic cations remain metallic down to low temperatures, and some even become superconducting under pressure.[1-4] Recent work within our group has concentrated on metal complexes of the type $(NH_yMe_{4-y})_n[M(dmit)_2]$ (y = 1 to 3; ; n = x, 1, 2; M = Ni, Pd, Pt; dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolato), several of which exhibit high room temperature conductivities and display metallic behaviour down to low temperatures.[5] From such work, and related studies[1-4] it is evident that small changes in the structure and composition of these complexes can greatly influence their properties. For a given complex, it is therefore interesting to discern the effect of the size and shape of the cation used on the intermolecular interaction network in derived compounds. With this in mind, we have carried out a study of metal complexes of the type $(NH_yR_{4-y})_n[M(dmit)_2]$ where M = Ni or Pd and R is a linear alkyl group. In the series where y = 2, the length of the R alkyl chains has been varied (C2 to C4) in order to understand the influence of the elongated cations on the structural arrangement of the $M(dmit)_2$ species. The influence of the size of the cation has been simultaneously studied by varying the number of alkyl groups from 2 to 3. In addition, we have also studied $(cation)_n[Ni(dmit)_2]$ complexes with cation = $(Ph_2I)^+$ (diphenyliodonium) and $(vinPh_2)^+$ (vinamidinium).

We have also extended the range of NIOS compounds derived from $M(dmit)_2$ complexes and open shell radical cations by using the symmetric or non symmetric donor molecules D1-D6 (Scheme 1) containing one or two TTF moieties.[6]



Scheme 1

On the other hand, $(BETS)_2(MX_4)$ salts (BETS = bis(ethylenedithio)tetraselenafulvanene; M = Ga, Fe, Co, Mn, Ni; X = Cl, Br) have been shown to exhibit unusual conducting and magnetic properties, including superconductivity and interaction between the BETS π conduction electrons and the localized anion spins on $(MX_4)^{n-}$.[7] We report here preliminary results on new compounds of this family with $(Cu_xCl_y)^{n-}$ and mixed $(FeCl_4)_{1-x}(GaCl_4)_x$ anions.

SYNTHESIS

The divalent (n = 2) and monovalent (n = 1) metal complexes $(\text{cation})_n[\text{M(dmit)}_2]$, M = Ni and Pd, were prepared according to published methods,[1,3] using appropriate counter cation salts. Elemental analyses were in agreement with the formula of the expected complexes. The $(\text{NHBu}_3)_2[\text{Ni(dmit)}_2]$ complex was further characterised by an X-ray structural determination (*vide infra*). In the case of the monovalent palladium complexes, however, oxidation of the divalent palladium complexes resulted, in each case, in the formation of a mixture of products, identified as the divalent, monovalent and non-integer oxidation state species. $(\text{Ph}_2\text{I})[\text{Ni(dmit)}_2]$ was prepared by cation exchange between $(\text{Ph}_2\text{I})\text{BF}_4$ and $(\text{NBu}_4)[\text{Ni(dmit)}_2]$.

The NIOS compounds, $(\text{cation})_x[\text{M(dmit)}_2]$, were grown on platinum electrodes by standard galvanostatic electrocrystallization techniques,[3] involving oxidation of either the corresponding monovalent $(\text{cation})[\text{Ni(dmit)}_2]$, or divalent $(\text{cation})_2[\text{Pd(dmit)}_2]$ complex. In the case of $(\text{vinPh}_2)_x[\text{Ni(dmit)}_2]$ the divalent $(\text{NBu}_4)_2[\text{Ni(dmit)}_2]$ was oxidized in the presence of an excess of $(\text{vinPh}_2)\text{BF}_4$.[8] Most of the experiments yielded microcrystalline powders at the anode. The elemental analyses of these powders indicate that the stoichiometry of the NIOS complexes approaches the value of x = 0.3.[9] In the case of $(\text{NHBu}_3)_x[\text{M(dmit)}_2]$ (M = Ni, Pd) and $(\text{vinPh}_2)_x[\text{Ni(dmit)}_2]$, crystals of up to 10 mm in length but with a thickness of less than 0.016 mm, were obtained. These crystals were suitable for temperature dependent conductivity studies but their quality was not sufficient for an X-ray crystal structure determination. Likewise, crystals of $(\text{Di})_x[\text{M(dmit)}_2]$ (i = 1-5; M = Ni, Pd), including crystals suitable for conductivities studies for i = 1, 2 and 4, were also obtained by galvanostatic oxidation of solutions of the appropriate neutral donor molecule Di and $(\text{NBu}_4)[\text{M(dmit)}_2]$. However, the best crystals were obtained by a combined electrocrystallization-diffusion method consisting in the preparation of the $(\text{Di})^+$ cation by electrochemical oxidation, followed by a slow-diffusion metathesis reaction with $(\text{NBu}_4)[\text{M(dmit)}_2]$. Electrocrystallization using the donor D6 and $(\text{NBu}_4)[\text{Ni(dmit)}_2]$ yielded crystals suitable for X-ray crystal structure determination. This study showed that the neutral $[\text{Ni(dmit)}_2]$ was unexpectedly obtained instead of the desired $(\text{D6})_x[\text{Ni(dmit)}_2]$ compound. The neutral $[\text{Ni(dmit)}_2]$ had already been obtained, unexpectedly as well, as an extraneous phase in the synthesis of $(\text{TTF})[\text{Ni(dmit)}_2]_2$ by slow diffusion.[10]

The $(\text{BETS})_4(\text{Cu}_2\text{Cl}_6)$ phase was prepared by standard galvanostatic electrochemical oxidation of solutions of BETS and $(\text{NEt}_4)_2(\text{CuCl}_4)$ in THF.[7c] Several $(\text{BETS})_n(\text{Cu}_x\text{Cl}_y)$ phases were obtained by the combined electrocrystallization-diffusion method from solutions of BETS and $(\text{AsPh}_4)(\text{CuCl}_3)$ or $(\text{NBu}_4)_2(\text{CuCl}_4)$ in chlorobenzene/ethanol (10 % vol.). The κ-$(BETS)_2(FeCl_4)_{1-x}(GaCl_4)_x$ phase was prepared by standard galvanostatic electrochemical oxidation of solutions of BETS and $(PPh_4)(FeCl_4)/(NBu_4)(GaCl_4)$ (1/1) in chlorobenzene/ethanol (10 % vol.).

X-RAY STRUCTURE OF $(NHBu_3)_2[Ni(dmit)_2]$[11]

The labelling and the packing of the $[Ni(dmit)_2]^{2-}$ and $(NHBu_3)^+$ ions are shown in Figure 1.

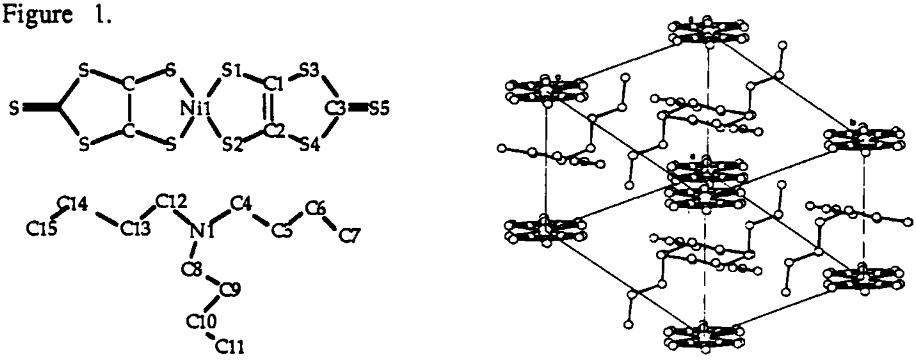


FIGURE 1 $(NHBu_3)_2[Ni(dmit)_2]$: the labelling and the packing of the $[Ni(dmit)_2]^{2-}$ and $(NHBu_3)^+$ ions

The unit cell contains one Ni(dmit) entity and one $(NHBu_3)^+$ cation. The Ni atom lies on an inversion center. The $Ni(dmit)_2$ units are nearly planar, the maximum deviation, observed for the S2 atom, being only 0.15 Å. The $Ni(dmit)_2$ intramolecular distances found in $(NHBu_3)_2[Ni(dmit)_2]$ are very similar to those found in $(NBu_4)_2[Ni(dmit)_2]$.[12] A pseudo-stacking arrangement of the $Ni(dmit)_2$ units appears along the [100] direction, the angle between the planes of these units and the *a* axis being 46.4°. Within these pseudo-stacks the $Ni(dmit)_2$ units are shifted along the long axis of the molecule by ≈ 7.3 Å and are separated by the $(NHBu_3)^+$ cations. The geometry and location of the cations accounts for the large distance (7.6 Å) observed between the planes of each of the $Ni(dmit)_2$ units.

X-RAY STRUCTURE OF $[Ni(dmit)_2]$[13]

The X-ray structure determination of $[Ni(dmit)_2]$ has already been published,[10] however, the results of the present study are slightly more accurate that the former ones. The main features of the structure are clearly shown on a projection along the *a* axis of the unit cell (Figure 2). The $[Ni(dmit)_2]$ molecules are centrosymmetric and planar. They are regularly stacked along the [010] direction and inclined with respect to this direction in such a way that the intermolecular spacing is 3.545 Å. The molecular planes of the molecules belonging to adjacent stacks are roughly perpendicular.

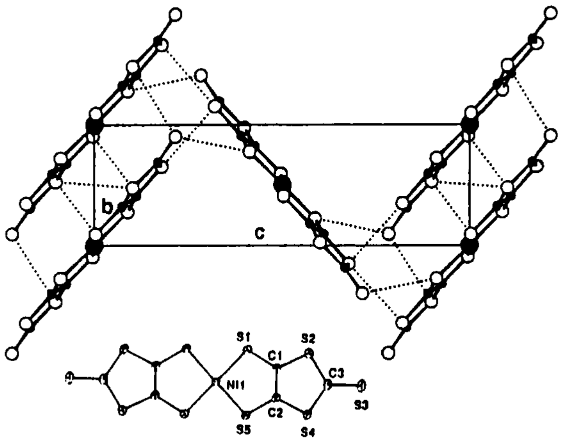
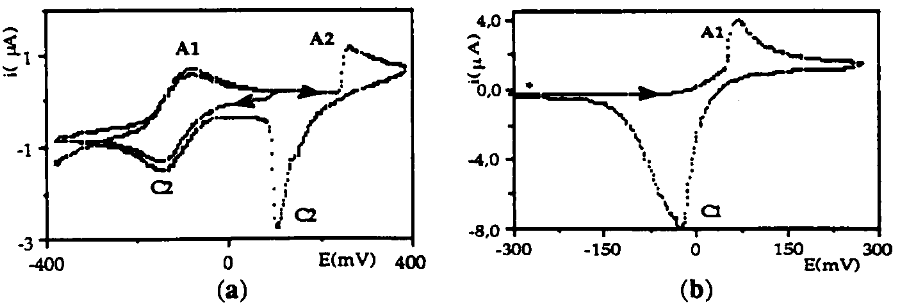


FIGURE 2 $[Ni(dmit)_2]$: projection of the structure along the *a* axis. Large black circles: Ni, grey circles: S, small black circles: C. Ni atoms are located at the corners and at the center of the unit cell. Thus the *x* coordinate of the central Ni atom of the drawing is shifted by 0.55*a* with respect to the other Ni atoms. Dotted lines indicate short (< 3.7 Å) S...S contacts.

ELECTROCHEMICAL STUDIES OF THE $(NH_yR_{4-y})_2[M(dmit)_2]$ COMPLEXES

The cyclic voltammograms of $(NH_2Pr_2)_2[M(dmit)_2]$ (M = Ni, Pd), presented in Figure 3, are representative of each of the metal complexes studied in this series.



(a)
(b)

FIGURE 3 Cyclic voltammogram of (**a**) $(NH_2Pr_2)_2[Ni(dmit)_2]$ and (**b**) $(NH_2Pr_2)_2[Pd(dmit)_2]$ (10^{-3} M) in $CH_3CN/(NH_2Pr_2)BF_4$ (10^{-1} M). Platinum electrode (1 mm diameter). Scan rate 0.1 $V.s^{-1}$

In the case of the nickel complexes (Figure 3a), if the potential scan is restricted to the first redox couple, the voltammogram presents the pattern of a quasi-reversible system. The second step, however, shows a rapid increase in the intensity of the anodic current as a function of the potential, consistent with deposition of an insoluble conductive species at the electrode surface, probably the non-integer oxidation state phase, $(cation)_x[Ni(dmit)_2]$, and the return peak is characteristic of a cathodic redissolution process.[14] Each of the nickel complexes displayed similar behaviour, showing very little cation dependence, and indicating that the preparation of non-integer oxidation state conducting species by electrochemical methods was possible.

In the case of the palladium complexes under the conditions employed, the two oxidation processes occur at approximately the same potential (Figure 3b), indicative of a weak on-site coulombic repulsion energy in the dianionic state.[15] This observation may also account for the difficulties encountered in obtaining the monovalent form of the palladium complexes by chemical oxidation. The return sweep results in a redissolution-type peak, or peaks, as observed for the analogous nickel complexes.

The electrochemical data for the $(NH_yR_{4-y})_2[M(dmit)_2]$ complexes are given in the additional material.

CONDUCTIVITY MEASUREMENTS FOR THE $(cation)_x[M(dmit)_2]$ COMPOUNDS

The conductivity of each of the $(NH_yR_{4-y})_2[M(dmit)_2]$ complexes obtained by electrocrystallization techniques was measured at room temperature on compressed pellets. All compounds exhibit moderate powder conductivities ranging from ≈ 0.05 to ≈ 2 S cm^{-1} (Additional material). These values compare well with those of previously studied $(NR_4)_x[M(dmit)_2]$,[1] and warrant further investigation.

No significant observation can be deduced by comparison of the conductivity values obtained for the $(NH_2R_2)_x[M(dmit)_2]$ type complexes and the $(NHR_3)_x[M(dmit)_2]$ analogues. In the absence of the crystal structures and single crystal conductivities of these compounds, it is not possible to discuss whether the difference in geometry between $(NH_2R_2)^+$ and $(NHR_3)^+$ cations would induce a modification in the molecular arrangement of the $M(dmit)_2$ units. Moreover, the study of $(NHBu_3)_x[Ni(dmit)_2]$ fully illustrates the difficulty in making any prediction on the single crystal conductivity value from that obtained on a compacted powder sample. In this latter case, the single crystal conductivity was determined and appeared to be an order of magnitude lower than that measured on the powder. This feature has been encountered in other molecular conductors and generally arises when the direction along which the conductivity is measured is not the same as the direction of highest conductivity. Temperature dependent four-probe conductivity measurements on this compound revealed it to be a semiconductor with an activation energy of 0.12 eV.

The room temperature single crystal conductivity of $(NHBu_3)_x[Pd(dmit)_2]$, on the other hand, shows it to be one of the most highly conducting (50 S cm^{-1}) NIOS $Pd(dmit)_2$ compounds known to date.[1] As a comparison, the conductivities of $(NBu_4)_x[Pd(dmit)_2]$ (x = 0.33 and 0.5) are 12 and 150 S cm^{-1}, respectively.[16] Below room temperature, the conductivity of $(NHBu_3)_x[Pd(dmit)_2]$ is thermally activated with an activation energy of 0.052 eV, typical of a small band gap semiconductor.

In the absence of crystal structures of both of these fractional oxidation state complexes, one can only speculate upon the reasons for their behaviour. As a first approximation from the electrochemistry data discussed above, it would appear that the on-site coulombic repulsion energy of the palladium complexes is much less than that of the analogous nickel complexes. The $[Pd(dmit)_2]^{x-}$ entities should therefore be more inclined to form stacks containing intermolecular interactions conducive to the formation of a conduction pathway. It is perhaps interesting to note that the analogous complexes $(NBu_4)_{0.29}[Ni(dmit)_2]$[10] and $(NBu_4)_x[Pd(dmit)_2]$ (x = 0.33 and 0.5)[16] exhibit similar behaviour; the nickel complex exhibits semiconducting behaviour and has a room temperature conductivity of 10 S cm^{-1}, whereas the palladium complexes are both metallic over limited temperature ranges.

The room temperature single crystal conductivity of $(vinPh_2)_x[Ni(dmit)_2]$ is 0.05 S cm^{-1} and this compound behaves as a semiconductor with a low activation energy of 0.04 eV.

Crystals of $(Di)_x[M(dmit)_2]$ (i = 1, 2, 4; M = Ni, Pd), suitable for conductivities studies, have been obtained. The room temperature single crystal conductivities of $(D2)_x[Ni(dmit)_2]$ and $(D4)_x[Ni(dmit)_2]$ are $4\ 10^{-2}$ and $2.\ 10^{-2}$ S cm^{-1}, respectively. These compounds exhibit semiconducting behaviors when decreasing the temperature. The room temperature single crystal conductivities of the palladium analogues, *i. e.*, $(D2)_x[Pd(dmit)_2]$ and $(D4)_x[Pd(dmit)_2]$, are much larger, 60 and 30 S cm^{-1}, respectively. Their temperature-dependent behavior exhibit several semiconducting regimes with low activation energies between 300 and ≈120 K (0.01, 0.02 eV, respectively), which increase between ≈120 and ≈80 K (0.14, 0.11 eV, respectively), and decrease again below 80 K (0.09, 0.06 eV, respectively). The $(D1)_x[Pd(dmit)_2]$ compound exhibits a similar behavior (30 S cm^{-1} at 300 K, 0.01 0.09 and 0.03 eV).

Most interesting is the very high room temperature conductivity of $(D1)_x[Ni(dmit)_2]$, 870 S cm^{-1}, *i. e.*, one of the highest ever reported for a molecule-based compound. When cooling the crystal, a metal-like behavior is observed (950 S cm^{-1} at 220 K). The conductivity saturates around 220 K and decreases below this temperature, indicating a thermally activated behavior with E_a =0.065 eV (Figure 4).

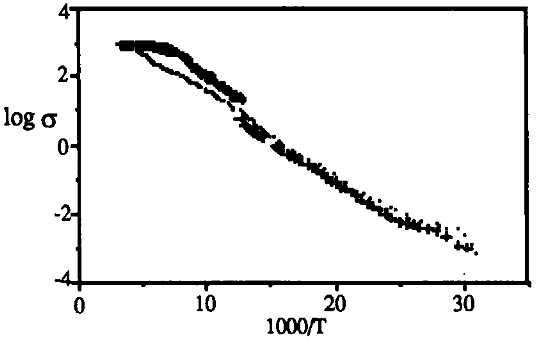


FIGURE 4 Temperature dependence of the conductivity of $(D1)_x[Ni(dmit)_2]$ (x, decreasing temperature; •, increasing temperature)

This transition seems to be quasi-reversible; when heating again the crystal it returns to a metallic state at ≈ 270 K. This quasi-reversible transition is observed on subsequent cooling and warming cycles. This behavior is reminiscent from that observed for the superconducting $(TTF)[Pd(dmit)_2]_2$ phases.[17]

When comparing the conducting behavior of the $(Di)_x[M(dmit)_2]$ with M = Ni or Pd, most of the Pd compounds exhibit higher conductivities than the Ni compounds, thus confirming a general trend observed in other series of $(cation)_x[M(dmit)_2]$ compounds. Nonetheless, the extremely conducting $(D1)_x[Ni(dmit)_2]$ compound seems to make an exception to this trend.

PROPERTIES OF BETS SALTS WITH $(Cu_xCl_y)^{n-}$ AND $(FeCl_4)_{1-x}(GaCl_4)_x$ ANIONS

A number of different phases of $(BETS)_n(Cu_xCl_y)$ were obtained when using either $(CuCl_4)^{2-}$ or $(CuCl_3)^-$ salts as supporting electrolytes. The needle-shaped $(BETS)_4(Cu_2Cl_6)$ phase, obtained with a $(CuCl_4)^{2-}$ salt, *i. e.*, $(NEt_4)_2(CuCl_4)$, in THF, is the best characterized (orthorhombic, *Pbcn*, a = 9.543(2), b = 34.897(8), c = 20.043(4) Å, V = 6674.2(3) Å^3, R = 0.085).[7c] The structure refinement shows a θ-type molecular arrangement, and the presence of $(Cu_2Cl_6)^{2-}$ dianions is clearly evidenced.[18] The room temperature single crystal conductivity is ≈ 10 S cm^{-1} and this compound remains metallic down to 4 K at least. The same phase, exhibiting similar conducting behavior and identical cell parameters has been obtained with a $(CuCl_3)^-$ salt, *i. e.*, $(AsPh_4)(CuCl_3)$, in chlorobenzene/ethanol.

Among several other phases with different morphologies, a block-shaped (thick hexagon) phase, has been obtained with $(AsPh_4)(CuCl_3)$ in chlorobenzene/ethanol. The cell parameters are: orthorhombic, *Pbnb*, $a = 8.477(8)$, $b = 11.703(3)$, $c = 35.031(8)$ Å. The structure refinement indicates the $(BETS)_4(Cu_4Cl_8)$ stoichiometry with $[Cl_2CuCl_2Cu]_n$ polymeric anion chains consisting of tetrahedral $(CuCl_4)$ units. This phase remains metallic down to 1.5 K. The detailed structures and properties of these and other $(BETS)_n(Cu_xCl_y)$ phases will be reported elsewhere.[18]

It has been recently reported that the λ-$(BETS)_2(FeCl_4)_{0.5}(GaCl_4)_{0.5}$ phase with a probably random distribution of disordered $(FeCl_4)^-$ and $(GaCl_4)^-$ anions undergoes a superconducting transition at 4.6 K.[7c] It should be noted that the presence of tris(oxalato)iron(III) magnetic ions does not prevent either the β''-$(BEDT\text{-}TTF)_4[(H_2O)Fe(C_2O_4)_3].C_6H_5CN$ salt from being superconductive ($T_C = 8.5$ K).[19] A new κ-type phase, with yet unknown stoichiometry, κ-$(BETS)_2(FeCl_4)_{1-x}(GaCl_4)_x$, has been obtained with $(PPh_4)(FeCl_4)/(NBu_4)(GaCl_4)$ (1/1) in chlorobenzene/ethanol. The room-temperature single-crystal conductivity of the κ-$(BETS)_2(FeCl_4)_{1-x}(GaCl_4)_x$ phase is 15-40 S cm^{-1} and most samples exhibits a 3000-fold increase in conductivity when lowering the temperature to 1.5 K. Cavity perturbation measurements on some samples of this phase give indication of a superconducting transition at ≈ 2.2 K, which remains to be confirmed. Moreover, Shubnikov-de Haas oscillations have been observed from which at least three frequencies, at 900, 2700 and 3600 Tesla, have been determined by Fourier analysis, corresponding to the 20, 60 and 80%, respectively, extremal cross-sections of the Brillouin zone (Figure 5).[20]

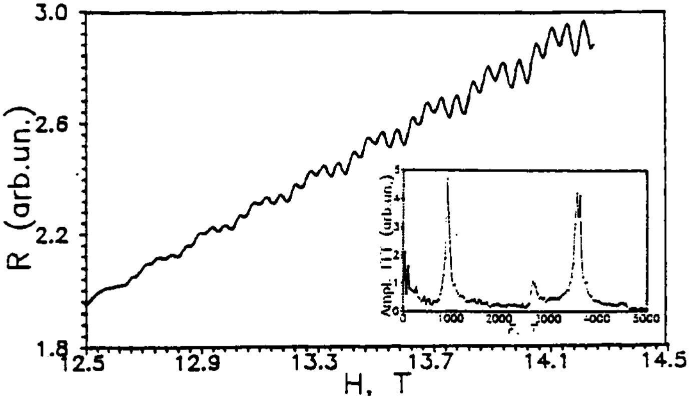


FIGURE 5 κ-$(BETS)_2(FeCl_4)_{1-x}(GaCl_4)_x$: Shubnikov-de Haas oscillations at 1.5 K. Insert shows the FFT analysis (from ref. 20).

Angle oscillations of the magnetoresistance of the κ-$(BETS)_2(FeCl_4)_{1-x}(GaCl_4)_x$ phase, reminiscent of those observed for the parent superconducting κ-$(BETS)_2(GaCl_4)$ phase,[21] have been also observed.[20]

CONCLUDING REMARKS

Further electrocrystallization experiments are needed and underway in an attempt to obtain crystals of the studied compounds, especially $(NHBu_3)_x[Pd(dmit)_2]$ and $(D1)_x[Ni(dmit)_2]$, of a suitable quality for an X-ray structural analysis in order to determine their true stoichiometries, to study their packing arrangement and to explain these observations more fully. Although certain members of the $M(dmit)_2$ family have been shown to exhibit metallic and even superconducting behavior,[3] the vast majority of metal complexes based on $M(dmit)_2$ complexes are semiconductors.[1] The work presented here thus underlines the delicate balance between the structure and composition of these materials that determines their solid state properties, and the difficulties in designing novel interesting conducting systems and in obtaining them as single crystals of sufficient quality for X-ray and physical studies. It is likely that progress and breakthroughs will still result in the future from serendipitous procedures rather than deliberate strategies.

This remark holds true in the case of all molecule-based conductors.[22] Indeed, the rather restricted range of superconducting compounds and the present levelling-off of T_c may suggest that this research is reaching some limits. However, it is well known that "plus une pierre tombe de moins haut et moins elle va plus vite" (the more a stone falls from a small height, the less its speed increases). Moreover, the preparation of new compounds, even non superconducting, may also lead to new concepts and theories,[23] which are another impetus for the continuation of this work. Indeed, this area is still very much alive after 15 years, as evidenced by the number of papers, reviews, books and scientific meetings (including the present 1995 PACIFICHEM Symposium) on this subject.

A new research direction which may lead to new classes of materials with novel properties has been identified, *i. e.*, electron transfer salts such as the $(BETS)_2(MX_4)$ systems exhibiting interactions between the conduction electrons and localized magnetic moments.[7] The superconductivity mechanism in such systems might differ from that observed in the previously studied compounds. Much work remains to develop this research to obtain a better understanding of the novel properties. Several mechanisms for magnetic-conducting systems have been proposed for describing the nature of the coupling between conduction electrons and localized moments,[7c] or for explaining the stabilization of the metallic state under high magnetic field in λ-$(BETS)_2FeCl_4$,[7b] or for understanding the existence of superconductivity in the presence of magnetic ions as in λ-$(BETS)_2(FeCl_4)_{0.5}(GaCl_4)_{0.5}$,[7c] and in β''-$(BEDT\text{-}TTF)_4[(H_2O)Fe(C_2O_4)_3].C_6H_5CN$,[19] but they must be verified.

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θ range of 1.5-30°; h = -14 to 14, k = -17 to 17, l = 0 to 11. Structure solved by direct methods (G. M. Sheldrick, SHELXS86 Program for Crystal Structure Solution, University of Göttingen, 1986) and refined by full-matrix least-squares and Fourier techniques using CRYSTALS (D. J. Watkin, J. R. Carruthers and P. W. Betteridge, CRYSTALS User's Guide, University of Oxford, 1988). All non-H atoms refined anisotropically. Positions of the H-atoms calculated (d_{N-H} = 1.03, d_{C-H} = 0.95 Å, and B = 1.3 B_{iso} (C or N atoms)), and refined . Final R = 0.037 and R_w = 0.039. Tables of atomic fractional coordinates with equivalent thermal parameters, interatomic distances and bond angles, and non-hydrogen atom anisotropic thermal parameters are provided as additional material available upon request to the editors or the authors.

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