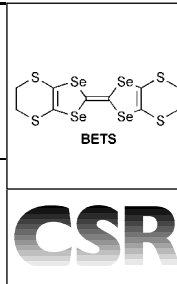


BETS as a source of molecular magnetic superconductors (BETS = bis(ethylenedithio)tetraselenafulvalene)[†]



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BETS-based salts (BETS = bis(ethylenedithio)tetraselenafulvalene) incorporating Fe³⁺ ions are most interesting candidate systems for the observation of interplay of conductivity and magnetism. Indeed, in λ -(BETS)₂FeCl₄, conduction electrons in the BETS layers do interact with spins localised on the (FeCl₄)⁻ anions. Systematic studies on (BETS)₂Fe_xGa_{1-x}Cl_{4-y}Br_y mixed-composition compounds, in which the electronic properties can be finely tuned by the chemical composition, have provided a number of interesting results, including the characterisation of a molecular antiferromagnetic metal, a conductor with an antiferromagnetic metal state at ambient pressure, and an anti-ferromagnetic superconductor. Unprecedented superconductor–insulator transitions and superconductor–metal transitions have been also observed.

1 Introduction

In molecule-based materials, it had been long believed that molecules kept their independence, even in the solid state. The

[†] In memory of Olivier Kahn.

electronic properties associated with intermolecular interactions were mostly ignored or not well understood. Thus, from the viewpoint of electronic functions, molecular crystals were considered to be irrelevant materials. In some cases, however, molecule-based solids were shown to exhibit properties, for example electrical and magnetic properties, which were quite distinct from those of the isolated molecules. The situation has now completely changed by virtue of the recent and enormous development in the fields of molecular conductors and magnets.¹ As a result, increasing attention is now being focused on the feasibility of making new types of electronic devices based on molecular systems. To meet this challenge, a better understanding of the electronic function of molecule-based solids is essential.

In *one-dimensional (1-D)* systems, such as most of the molecular organic conductors studied in 1970s after the discovery of the archetypal (TTF)(TCNQ) compound (TTF = tetrathiafulvalene; TCNQ = tetracyano-*p*-quinodimethane; Fig. 1),² the molecules are stacked and interacting along one direction through their delocalised π system. No electronic interaction is observed between molecules of adjacent stacks. Electronic instabilities resulting in metal–insulator transitions encountered upon cooling, such as for example the ubiquitous Peierls transition associated with a lattice distortion,³ are

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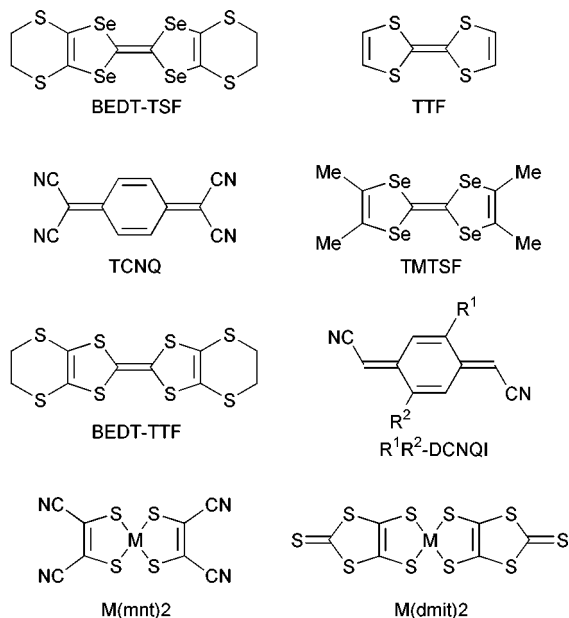


Fig. 1 Precursor molecules to conducting and superconducting molecule-based compounds.

generally observed in *1-D* systems and prevent them from undergoing a superconducting (SC) transition.

The first molecule-based superconductor (TMTSF)₂PF₆ (TMTSF = tetramethyltetraselenafulvalene; see Fig. 1) was reported in 1980.⁴ Examination of its crystal structure and extended Hückel tight-binding electronic band structure calculations⁵ provided an important guideline for the design of *two-dimensional* (*2-D*) molecular metals and superconductors. In (TMTSF)₂PF₆, stronger interactions between the stacks evidenced by short Se...Se interatomic distances are observed. Thus the structure of (TMTSF)₂PF₆ can be no longer considered as *1-D*, but rather as quasi *1-D* or *2-D*. Following up the resulting guideline, which consists of enhancing interstack interactions by using multi-chalcogen π molecules, extensive studies were carried out to develop new types of *2-D* systems and contributed greatly to the production of a number of molecular metals and superconductors.^{1,2} One of the initial goals of this research was the realisation of ideally *2-D* organic metals with a superconducting ground state. This goal was reached when the electronic band structure calculations of β -(BEDT-TTF)₂I₃ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene),⁶ and especially that of κ -(BEDT-TTF)₂I₃,⁷ the first superconductor exhibiting the characteristic *2-D*, κ -type molecular arrangement (in which the molecules are not even stacked), were reported (β and κ designate the characteristic type of packing of the molecules in the crystal structure; other types of packing are designated as α , θ , γ , δ , λ , etc.⁸). The phase exhibiting the highest superconducting critical temperature T_c (12.8 K at 0.3 kbar), κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl, belongs to this κ -type BEDT-TTF-based series. A detailed review on BEDT-TTF-based systems is available.⁸

During the same period, a parallel research effort was devoted to the design and preparation of molecule-based ferromagnets. After the discovery in 1985 of the first molecule-based ferromagnet, [Fe(C₅Me₅)₂](TCNE) (TCNE = tetracyanoethylene), several additional series were introduced, including systems having ordering temperatures above room temperatures such as V(TCNE)_x·y(solvent).¹

To sum up, until recently, one of the main goals in the chemistry of molecular solids was the preparation and characterisation of molecule-based superconductors or ferromagnets. Nowadays, however, one may consider that molecule-based superconductors and ferromagnets have become non-rare materials.¹ Now, the development of multi-functional molec-

ular systems, such as magnetic conductors and superconductors, has evolved as the new challenge.

In these systems, the coexistence of both magnetic and electrical properties, and better still an actual interplay between conduction electrons and localised magnetic moments incorporated in the molecule-based material, is much sought after. Indeed, there was no example of a molecule-based superconductor in which magnetic ordering and superconductivity coexist. Moreover, though non-molecular magnetic superconductors have been known for more than 20 years, the number of such systems having a T_c lower than the Neel temperature, T_N is quite limited. For some BETS-based superconductors, which will be discussed in this review, the superconducting transition does occur in the presence of a local field (magnetic ordering). Consequently, a perfect Meissner state may be not realised in these systems and this may explain the novelty of their superconducting transition. Therefore, the stimulus for this research is twofold: the possible development of new concepts in the physics of condensed matter and, as mentioned above, the making of new types of electronic devices. Although promises bind only those who listen to them, one could envision the fabrication of a device built around a metamagnetic superconductor with a small critical field that would allow the superconducting state to be switched on and off. For this purpose, the 'designability' of molecules makes molecule-based systems especially suitable for preparing multifunctional materials by combining different functional groups in a single molecular unit.

After a brief recollection on the early development of molecule-based magnetic conductors (Section 2), on BETS and BETS-based salts synthesis and attributes, and on the seminal discovery of the field-restoration of a highly conducting state in the λ -(BETS)₂FeCl₄ phase (Section 3), we will review (Sections 4–7) the results obtained when studying (BETS)₂Fe_xGa_{1-x}Cl_{4-y}Br_y mixed-composition phases, including the characterisation of new non-magnetic superconductors and of the first molecular antiferromagnetic superconductor, and the observation of unprecedented superconductor–insulator (SC-I) transitions and superconductor–metal (SC-M) transitions.

2 Early developments of molecule-based magnetic conductors

As far as the coupling of conduction electrons and localised magnetic moments is concerned, the (DMe-DCNQI)₂Cu compound reported in 1986 (DMe-DCNQI = dimethyl dicyanoquinonediimine)⁹ seemed very promising. The mixed-valence of the copper atom drew, for the first time in a molecule-based conductor, the attention to the existence of a π -d mixing band.¹⁰ However, the coexistence of the π conduction electrons and magnetic moments was not realised in (DMe-DCNQI)₂Cu and derived systems. Indeed, the magnetic properties of Cu²⁺ could be observed only in the insulating state where a [Cu⁺Cu⁺Cu²⁺]_∞ threefold arrangement occurs.¹⁰ Nevertheless, the development of magnetic conductors in which π conduction electrons and magnetic moments may coexist at low temperature became in the late 1980s one of the new targets in the development of new molecule-based conductors.

An interesting one-dimensional conduction model has been proposed based on metal phthalocyanine molecules. It was expected that in these systems magnetic ions such as Co²⁺ and Cu²⁺ could be strongly coupled with the π conduction electrons.¹¹ However, due to the Peierls instability, none of the *1-D* metal phthalocyanine-based conductors studied retain their metallic state down to low temperature.

Coupled one-dimensional electronic and magnetic properties have been reported in (perylene)[M(mnt)₂] complexes (M =

Ni, Pd, Pt; mnt^{2-} = maleonitriledithiolato; see Fig. 1).¹² In these systems, a large paramagnetic susceptibility is due to the large paramagnetic contribution from the Ni(mnt)₂ component in addition to the Pauli susceptibility from π conduction electrons in the perylene chains. At low temperatures, Peierls and spin-Peierls^{1,3} transitions simultaneously take place in the conduction (perylene) and magnetic ($\text{M}(\text{mnt})_2$) chains, respectively, but the existence of a real interplay is not yet established.

The only molecular superconductors based on transition metal complexes are derived from $\text{M}(\text{dmit})_2$ (dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolato; see Fig. 1).¹³ In most of the $\text{M}(\text{dmit})_2$ -based compounds the oxidation state of the metal (Ni, Pd, Pt) remains M^{2+} whatever the global non-integral oxidation state of the $[\text{M}(\text{dmit})_2]^{x-}$ component, and no unusual magnetic properties are observed. Recently, however, the first ferromagnet in this class of compounds, $[\text{Mn}(\text{C}_5\text{Me}_5)_2][\text{Ni}(\text{dmit})_2]$, obtained by associating the magnetic $[\text{Mn}(\text{C}_5\text{Me}_5)_2]^+$ cation has been reported.¹⁴

Instead of associating an acceptor molecule-based anion with a magnetic cation as in the two previous examples, one might as well incorporate an appropriate magnetic anion in a donor molecule-based conducting salt. In the 1-D $(\text{TMTSF})_2\text{X}$ -like salts, where the anions X are located between the conduction layers formed by the planar π -delocalised TMTSF molecules, the interaction between the π conduction electrons and the localised magnetic moments of anions containing 3d orbitals is not expected to be very strong because there is no possible direct overlap between the wave function of the π electrons and the magnetic 3d orbitals. Therefore the electronic properties reflecting π -d interaction should be observable only at very low temperature. By contrast, 2-D salts derived from BEDT-TTF-like donor molecules, exhibiting metal-like properties down to low temperatures, and possibly becoming superconducting appeared to be more promising candidate systems for the preparation of molecule-based magnetic conductors and superconductors.

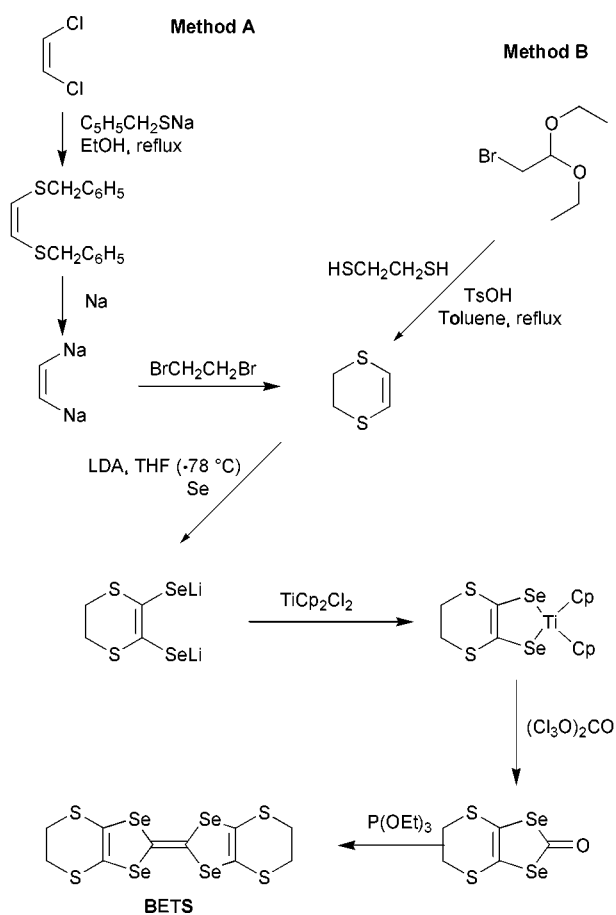
The first reported donor molecule-based conductor incorporating paramagnetic ions and exhibiting a stable metallic state and a weak ferromagnetic interaction between Cu^{2+} ions was $(\text{BEDT-TTF})_3\text{CuCl}_4 \cdot \text{H}_2\text{O}$.¹⁵ In 1995, the first paramagnetic organic superconductor, $\beta''\text{-(BEDT-TTF)}_4(\text{H}_3\text{O})[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot (\text{C}_6\text{H}_5\text{CN})$ was discovered.¹⁶

Examination of a series of BETS-based conducting salts (BETS = bis(ethylenedithio)tetraselenafulvalene) associated with various anions showed these salts had a strong tendency to possess stable metallic states.^{17–20} Finally, such BETS-based salts incorporating Fe^{3+} ions appeared to be most interesting candidate systems for the observation of interplay of conductivity and magnetism and for the preparation of magnetic conductors and superconductors.

3 The BETS molecule and derived salts

The BETS molecule is a modification of BEDT-TTF obtained by substituting selenium for sulfur in the central tetrathiafulvalene fragment (See Fig. 1). After the first syntheses of BETS, involving H_2Se or CSe_2 as selenium sources and/or the functionalisation of tetraselenafulvalene,¹⁷ a less hazardous synthetic procedure using selenium powder was developed (Scheme 1, Method A).¹⁸ In order to avoid the use of malodorous benzylmercaptan, to reduce the number of reaction steps, and to increase yields, this procedure was further improved: a convenient one-step reaction for the preparation of 2,3-dihydro-1,4-dithiin was perfected (Scheme 1, Method B).²¹

Although BETS is strictly isostructural to BEDT-TTF, some differences in the molecular structures of BETS and BEDT-TTF



Scheme 1

indicate that the shape of BETS is more suitable for a good transverse overlap than BEDT-TTF or BEST (BEST = bis(ethylenediseleno)tetrathiafulvalene).^{18,19,21} Indeed, most of the *ca.* 70 BETS-derived salts prepared so far exhibit metal-like behaviour and more than 10% of them undergo a SC transition.²² This does not reduce the merit of BEDT-TTF (more than 20 BEDT-TTF-based superconducting phases have been characterised so far),⁸ and not even that of BEST since a new superconductor, $\kappa\text{-(BEST)}_2\text{CuN}(\text{CN})_2\text{Br}$, has been recently discovered.²³

$(\text{BETS})_2\text{A}$ salts are typically prepared by electrocrystallisation from solutions of BETS and a salt of the appropriate anion A^- . As an example, the structure of the isostructural $\lambda\text{-(BETS)}_2\text{MCl}_4$ ($\text{M} = \text{Ga}, \text{Fe}$) is shown in Fig. 2.^{19,20} Extended Hückel tight binding band calculation and the resulting two-dimensional cylindrical Fermi surfaces confirm the two-dimensional nature of both compounds.^{20,24}

The seminal finding on an interplay between π conduction electrons and localised magnetic moments was made in the early 1990s when the transport properties of the above mentioned $\lambda\text{-(BETS)}_2\text{FeCl}_4$ and $\lambda\text{-(BETS)}_2\text{GaCl}_4$ phases were reported.¹⁹ The iron-based phase with the magnetic $(\text{FeCl}_4)^-$ anion undergoes a sharp metal-insulator transition (MI) at ≈ 8 K. By contrast, the isostructural gallium-based analogue with the non-magnetic $(\text{GaCl}_4)^-$ anion undergoes a SC transition around 6 K. One could suspect that the behaviours of these phases may be related to, or at least influenced by the presence or absence of the spins localised on the Fe^{3+} ions. Indeed, application of magnetic fields led to unexpected results in the conducting behaviour of $\lambda\text{-(BETS)}_2\text{FeCl}_4$.²⁴ With increasing field, the resistivity minimum associated with the MI transition observed at *ca.* 10 K is shifted towards low temperatures and is suppressed for a field higher than 10 Tesla.

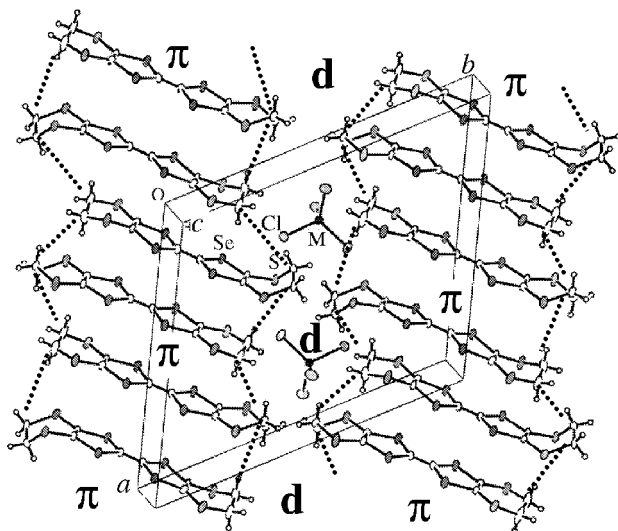


Fig. 2 Crystal structure of λ -(BETS)₂MCl₄ (M = Fe, Ga) with triclinic lattice. The lattice constants are: λ -(BETS)₂GaCl₄, $a = 16.172$, $b = 18.616$, $c = 6.607$ Å, $\alpha = 98.38$, $\beta = 96.75$, $\gamma = 112.56^\circ$; λ -(BETS)₂FeCl₄, $a = 16.164$, $b = 18.538$, $c = 6.593$ Å, $\alpha = 98.40$, $\beta = 96.67$, $\gamma = 112.52^\circ$.

From this seminal finding forward, a large research effort involving a number of physical and theoretical studies, including pulse-field magnetoresistance measurements, ESR and antiferromagnetic resonance, SQUID static magnetic susceptibility and magnetisation measurements, cantilever magnetometry and theoretical fermiology have elucidated the actual nature of the insulating low-temperature state of λ -(BETS)₂FeCl₄ and the mechanism of restoration of the metallic state by application of a magnetic field (FRHCS, *i.e.*, field-restored highly conducting state). The results of this research are described in a detailed article,²⁴ and can be summarised by the temperature–magnetic field diagram²⁵ shown in Fig. 3. At

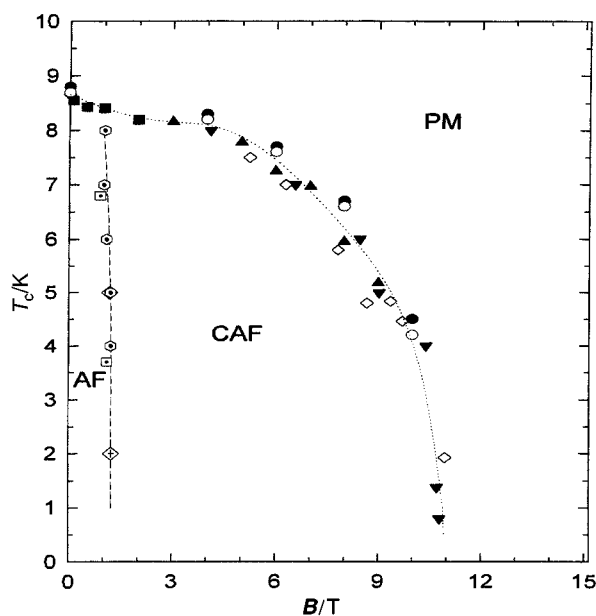


Fig. 3 Temperature–magnetic field diagram of λ -(BETS)₂FeCl₄. Reproduced with permission from ref. 24.

high temperature and low field the compound is paramagnetic and metallic (PM). With decreasing temperature at low field, an antiferromagnetic (AF) transition co-operatively takes place at the MI transition temperature, T_{MI} . Below T_{MI} , a π – d coupled AF insulating state is observed; in this AF state and for fields less than 1 Tesla, the spins are anti-parallel. When the field is higher than ≈ 1 Tesla, because of a spin–flop transition, the

spins become increasingly canted (CAF). Finally, the restoration of a paramagnetic metallic state results from the progressive canting of the spins on the (FeCl₄)[−] anion chains and the progressive alignment of the spins induced by higher magnetic fields.

Thus, λ -(BETS)₂FeCl₄ can be regarded as the first example of a molecular conductor exhibiting colossal magnetoresistance (CMR). Moreover, by applying pressure, the AF insulating state is also suppressed, and a SC transition is observed above 2.5 kbar.²⁶

In conclusion at this point, λ -(BETS)₂FeCl₄ is a conducting molecule-based salt in which conduction electrons do interact with localised spins. Following on from this outcome, systematic studies on (BETS)₂Fe_xGa_{1−x}Cl_{4−y}Br_y mixed-composition compounds were carried out and provided a number of interesting results, which will be reviewed, in the following sections.

4 Superconducting transition in λ -(BETS)₂GaCl_{4−y}Br_y and λ -(BETS)₂GaCl₃F

λ -type BETS-based salts incorporating non-magnetic Ga tetrahalide anions may be considered as forming the ‘standard’ π electron compounds whose properties can be compared with those of the corresponding salts associated with magnetic, *e.g.*, Fe³⁺, anions.

The mixed tetrahalide λ -(BETS)₂GaCl_{4−y}Br_y and λ -(BETS)₂GaCl₃F salts are isostructural to pure λ -(BETS)₂GaCl₄ (see Fig. 2). The unit cell volume of λ -(BETS)₂GaCl_{4−y}Br_y increases almost linearly when increasing the Br-content (y -value).²⁷ Consequently, an effective ‘negative chemical pressure’ will be produced in the crystal, which tends to make the system semiconducting. Indeed, the physical properties of the λ -(BETS)₂GaCl_{4−y}Br_y phases change continuously with changing Br/Cl ratio. Fig. 4a shows the y -dependence of the resistivity

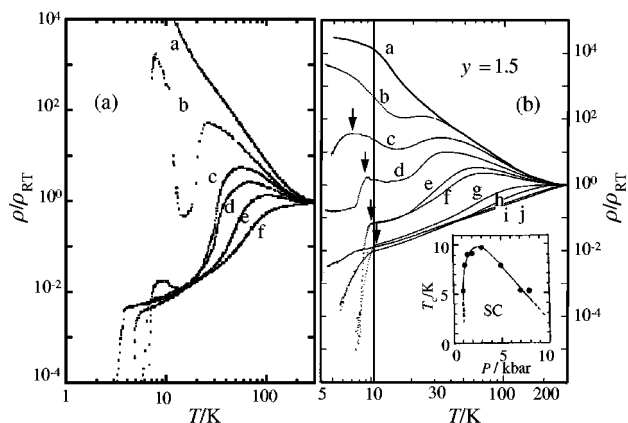


Fig. 4 (a) Temperature dependence of the normalised resistivities of λ -(BETS)₂GaCl_{4−y}Br_y (a–e) and λ -(BETS)₂GaCl₃F (f): $y = 1.5$ (a), 0.7 (b), 0.5 (c), 0.3 (d) and 0.0 (e). The room temperature resistivity of λ -(BETS)₂GaCl₄ is 0.03 Ω cm. (b) Temperature dependence of the resistivity of λ -(BETS)₂GaCl_{2.5}Br_{1.5} at pressures of 1 bar (a), 1.0 kbar (b), 1.05 (c), 1.25 (d), 1.5 (e), 2.0 (f), 3.0 (g), 5.0 (h), 7.0 (i), 9.0 (j). The insert is the pressure dependence of T_c (redrawn after ref. 27).

behaviour. When increasing the Br-content, T_c is enhanced from 5.5–6 K ($y = 0$) to 7–8 K ($y \approx 0.7$). For $y > 0.8$, the corresponding phases show semiconducting properties for the whole temperature range. This is probably due to the strong correlation of π conduction electrons, which also explains the presence of the round resistivity maximum observed for compounds with lower Br-content. The y -dependence of the resistivity behaviour can be reproduced by applying ‘real pressure’ to a semiconducting λ -(BETS)₂GaCl_{4−y}Br_y phase. For $y = 1.5$ for example (Fig. 4b), the SC transition appears at

high pressure (> 2 kbar) and T_c reaches its maximum of ≈ 10 K at 3 kbar. At higher pressure (> 5 kbar), the compound remains metallic down to low temperature. In conclusion, fine tuning of the electrical properties within the λ -(BETS) $_2$ GaCl $_{4-y}$ Br $_y$ system may be controlled by the chemical composition.²⁷

5 π -d Coupling in λ -(BETS) $_2$ FeCl $_{4-y}$ Br $_y$. The first molecular antiferromagnetic metal

When increasing the Br-content within the λ -(BETS) $_2$ FeCl $_{4-y}$ Br $_y$ series, the resistivity maximum associated with the strong correlation of π conduction electrons becomes more prominent and the MI transition temperature is increased (Fig. 5a).²⁸ For $y \approx 0.8$, a semiconducting behaviour is observed over the whole temperature range (< 300 K). The same features are observed when applying 'real pressure' to the semiconducting Br-rich λ -(BETS) $_2$ FeCl $_{3.2}$ Br $_{0.8}$ (Fig. 5b).

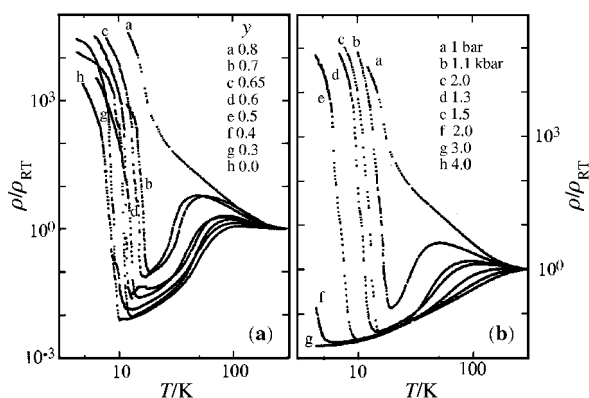


Fig. 5 (a) Temperature dependence of the normalised resistivities of λ -(BETS) $_2$ FeCl $_{4-y}$ Br $_y$. (b) Temperature dependence of the resistivity of λ -(BETS) $_2$ FeCl $_{3.2}$ Br $_{0.8}$ at various pressures (redrawn after ref. 28).

Since the Fe $^{3+}$ ions are in a high spin state ($S = 5/2$), the contribution of the conduction electrons to the magnetic susceptibility is negligible. Fig. 6 shows the temperature dependence of the susceptibility of oriented thin needle crystals of two λ -(BETS) $_2$ FeCl $_{4-y}$ Br $_y$ phases with $y = 0$ and 0.65 . In λ -(BETS) $_2$ FeCl $_4$, a sharp drop is observed at T_{MI} when the field is applied parallel to the c axis. This drop (7–8 %) can be regarded as evidence for the appearance of localised π spins ($S = 1/2$) on BETS dimers and the development of a π -d coupled AF insulating structure below T_{MI} . The easy axis of the AF spin structure is approximately parallel to the c axis and the spin-flop field is about 1 T.^{24,29}

When increasing the Br-content within the λ -(BETS) $_2$ FeCl $_{4-y}$ Br $_y$ series up to $y = 0.3$ – 0.4 , the direction of the field showing a sharp drop of susceptibility is changed from a direction approximately parallel to the c axis to the perpendicular direction. Simultaneously, the susceptibility drop observed for low Br-contents at $H\parallel c$ lessens and disappears for $y > 0.5$, upon which a susceptibility drop is observed for $H\perp c$.²⁸ These gradual changes suggest that the coupling between π and d electrons weakens with increasing Br-content. These and other data^{28,29} may be summarised by the temperature–composition phase diagram of the λ -(BETS) $_2$ FeCl $_{4-y}$ Br $_y$ series shown in Fig. 7. At low temperatures, there are three AF insulating phases: a π -d coupled AF insulating phase for low Br-contents (I), an intermediate phase where the coupling between π and d electrons decreases and the easy axis of AF spin structure rotates from the direction approximately parallel to the c axis to the perpendicular direction (II), and, for high Br-contents, an insulating phase where π and d electrons are uncoupled (III).

As previously mentioned, the MI transition of λ -(BETS) $_2$ FeCl $_4$ is suppressed with increasing pressure and disappears

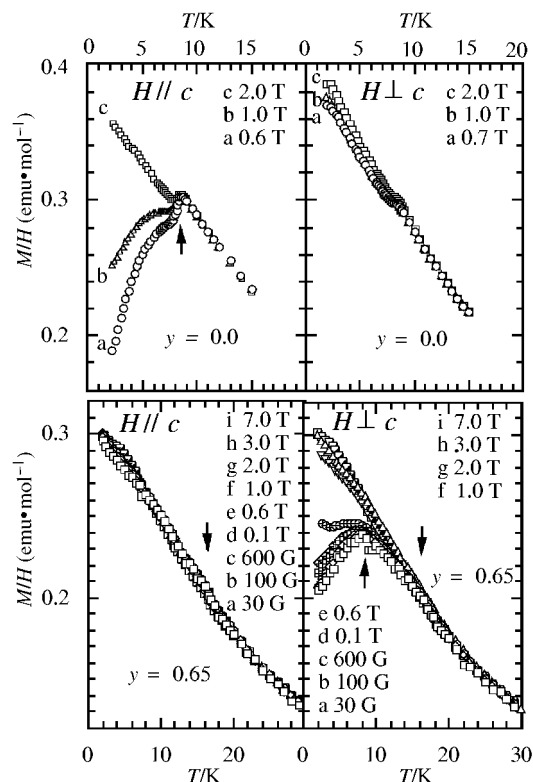


Fig. 6 Temperature dependence of the susceptibility of two λ -(BETS) $_2$ FeCl $_{4-y}$ Br $_y$ phases with $y = 0$ and 0.65 for fields parallel and perpendicular to axis c (redrawn after ref. 28). For $y = 0$, the arrow indicates the cooperative MI and AF transition temperature. For $y = 0.65$, up and down arrows indicate the AF and MI transition temperatures (T_N, T_{MI}), respectively.

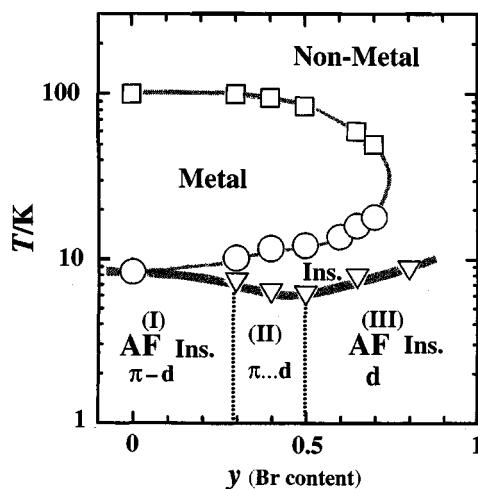


Fig. 7 Temperature–composition phase diagram of λ -(BETS) $_2$ FeCl $_{4-y}$ Br $_y$.²⁸ The squares indicate the temperature corresponding to the resistivity maximum (see Fig. 5), the circles correspond to T_{MI} (see Fig. 5), and the triangles indicate the temperature of the Fe $^{3+}$ spin ordering (see Fig. 6).

above 3.5–4 kbar. High pressure susceptibility measurements show that the coupling between π and d electrons decreases and disappears when applying pressure.³⁰ Features, reminiscent of those observed in the λ -(BETS) $_2$ FeCl $_{4-y}$ Br $_y$ series when increasing the Br-content, are observed even at 5 kbar where the MI transition is completely suppressed. Therefore, π conduction electrons and antiferromagnetically ordered Fe $^{3+}$ spins of λ -(BETS) $_2$ FeCl $_4$ seem to coexist in the high-pressure range. Consequently, λ -(BETS) $_2$ FeCl $_4$ may be considered as the first molecule-based conductor with an AF metallic phase at low temperature. Furthermore, this compound undergoes a SC transition above 3 kbar (Fig. 8).²⁶ On combining these data, the

temperature–pressure phase diagram of λ -(BETS)₂FeCl₄ may be drawn (insert in Fig. 8). With increasing pressure, the coupling between π and d electron systems weakens, resulting in a progressive AF ordering of the Fe³⁺ spins and a restoration of the metallic state. The π conduction electrons in this pressure-induced restored metallic state undergo a SC transition at lower temperature.

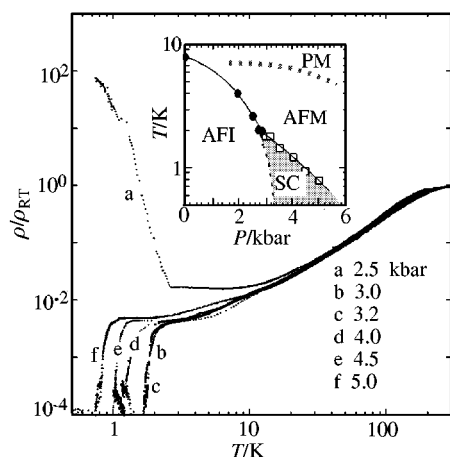


Fig. 8 Temperature dependence of the resistivity of λ -(BETS)₂FeCl₄ at high pressures. The insert shows the temperature–pressure phase diagram. AFI = antiferromagnetic insulating phase, SC = superconducting phase, and AFM = antiferromagnetic metal phase (redrawn after ref. 26).

6 Unprecedented superconductor–insulator transitions in the λ -(BETS)₂Fe_xGa_{1-x}Cl_{4-y}Br_y series

Let us recall that the λ -(BETS)₂FeCl₄ phase with the magnetic (FeCl₄)⁻ anion undergoes a MI transition, whereas the λ -(BETS)₂GaCl₄ isostructural analogue with the non-magnetic (GaCl₄)⁻ anion undergoes a SC transition at the same temperature. One might wonder what amount of iron would suppress superconductivity in a mixed λ -(BETS)₂Fe_xGa_{1-x}Cl₄ phase.

Crystals of λ -(BETS)₂Fe_xGa_{1-x}Cl₄ were prepared electrochemically from 10% ethanol-containing chlorobenzene solutions of BETS and mixed (Et₄N)(FeCl₄) and (Et₄N)(GaCl₄) supporting electrolytes in the appropriate proportions. The x -values were determined by EPMA (electron probe microanalysis) and were in a good agreement with the Fe/Ga ratio in the starting solution, except for $x < 0.2$ and $x > 0.8$ where the minority component (Fe³⁺ for $x < 0.2$, and Ga³⁺ for $x > 0.8$) tended to be included in the crystal.

The Fe-rich phases underwent a sharp MI transition. The transition temperature T_{MI} decreased with increasing Ga-content. By contrast, the Ga-rich phases exhibited a SC transition. T_c decreased slightly with increasing Fe-content. At the border line, when x was slightly smaller than 0.5, the compound still underwent a SC transition, that was followed by an unprecedented superconductor–insulator (SC-I) transition at lower temperature, *i.e.*, below liquid helium temperature (Fig. 9).³¹ Unlike a standard SC transition, this SC-I transition exhibited an hysteresis, indicating it to be first order (insert in Fig. 9).

Fig. 10 shows the temperature–composition phase diagram in the λ -(BETS)₂Fe_xGa_{1-x}Cl₄ series. For $x > 0.5$, the phases undergo a MI transition. For $x < 0.35$, the phases possess a superconducting ground state. Sequential SC and SC-I transitions are observed for $0.35 < x < 0.5$.

A very large diamagnetic susceptibility of the Ga-rich phases below T_c indicates the bulk nature of the superconducting state,

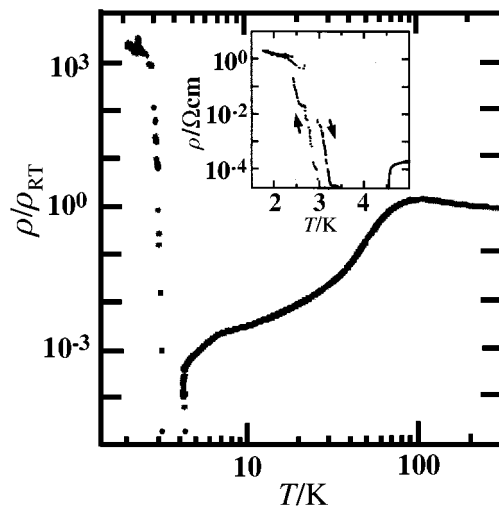


Fig. 9 Unprecedented SC-I transition observed for the λ -(BETS)₂-Fe_{0.45}Ga_{0.55} phase (redrawn after ref. 26).

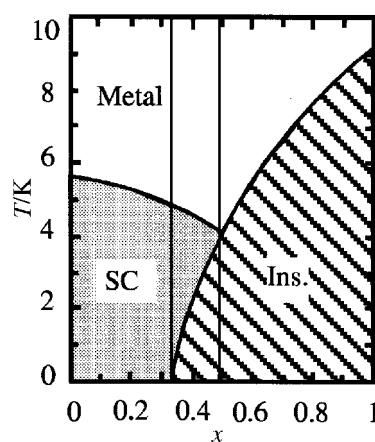


Fig. 10 Temperature–composition phase diagram in the λ -(BETS)₂Fe_xGa_{1-x}Cl₄ series (redrawn after ref. 31).

even near the phase boundary around $x = 0.5$. This was confirmed by *ac* susceptibility measurements of λ -(BETS)₂Fe_{0.47}Ga_{0.53}Cl₄.³¹ For $x > 0.35$, a spin–flop transition is observed at 2 K and 0.6 T when the field is parallel to the c axis, indicating a π –d coupled AF insulating state similar to that (see above) of the pure λ -(BETS)₂FeCl₄ phase.³¹ Moreover, application of high pressure (> 2.5 kbar for the Fe-rich λ -(BETS)₂Fe_{0.9}Ga_{0.1}Cl₄ phase) suppresses this insulating state and induces a SC transition.

We have already mentioned (see Section 4) that substituting Br for Cl atoms results in an effective negative pressure in the crystal lattice. As in the λ -(BETS)₂MCl_{4-y}Br_y series ($M = \text{Fe}$ or Ga), the λ -(BETS)₂Fe_xGa_{1-x}Cl₃Br phases exhibit a semi-conducting behaviour associated with the strong electron correlation due to the large Br-content. At 1.8 kbar, however, the λ -(BETS)₂Fe_{0.5}Ga_{0.5}Cl₃Br phase shows both SC and SC-I transitions (7 and 3.5 K, respectively). As in the Br-rich λ -(BETS)₂GaCl_{4-y}Br_y system, T_c occurs quite a bit higher than in λ -(BETS)₂GaCl₄. Consequently, the temperature range in which a superconducting λ -(BETS)₂Fe_xGa_{1-x}Cl₃Br phase may be observed is quite expanded between high temperatures for which this phase is metallic and low temperatures for which this phase is insulating. Furthermore, when the Fe-content becomes small ($x < 0.2$), the λ -(BETS)₂Fe_xGa_{1-x}Cl₃Br phases exhibit a SC-M transition at 7 K and 1.6 kbar.³² In spite of the small Fe-content, the magnetic susceptibility measurements show an AF behaviour. For these low Fe-content phases, there seem to be two metal states at 1.5 kbar neighbouring a superconducting state. It is thus highly possible that the π –d interaction and AF ordering of Fe³⁺ spins play essential roles in suppressing

superconductivity in this system. Clearly, the mixed λ - $(\text{BETS})_2\text{Fe}_x\text{Ga}_{1-x}\text{Cl}_{4-y}\text{Br}_y$ series deserves further work.

7 An antiferromagnetic molecular superconductor κ - $(\text{BETS})_2\text{FeBr}_4$

Two κ -type BETS-based superconductors, κ - $(\text{BETS})_2\text{MBr}_4$ ($M = \text{Ga}, \text{Fe}$), have been recently reported.^{33,34} Let us recall that, unlike the λ -type salts with a fourfold quasi-stacked structure of donor molecules, in κ -type structures the donor molecules are no longer stacked, but form face-to-face dimers rotated by about 90° with respect to each other.^{7,8} The plate-shaped crystals of κ - $(\text{BETS})_2\text{MBr}_4$ belong to the orthorhombic system with space group $Pnma$ (for $M = \text{Fe}$, the lattice constants are $a = 11.787$, $b = 36.607$, $c = 8.504$ Å; Fig. 11). The two-dimensional conduction layers composed of the BETS dimers and the MBr_4 layers are arranged alternately along the b axis.

Both κ - $(\text{BETS})_2\text{FeBr}_4$ and κ - $(\text{BETS})_2\text{GaBr}_4$ show a weakly metal-like behaviour down to ≈ 200 K. Below this temperature a characteristic round resistivity maximum is observed at 60–70 K (Fig. 12). In the case of κ - $(\text{BETS})_2\text{GaBr}_4$, a rapid resistivity decrease is observed below 50 K, and finally a broad SC transition takes place with a T_c of 1.0–0.5 K.³⁴

Except for the low temperature region, the resistivity behaviour of κ - $(\text{BETS})_2\text{FeBr}_4$ is essentially the same as that of κ - $(\text{BETS})_2\text{GaBr}_4$, indicating a close resemblance of the π electron states of both systems. At low temperatures, κ - $(\text{BETS})_2\text{FeBr}_4$ exhibits novel physical properties due, again, to the interplay between π and 3d magnetic moments localised on the Fe^{3+} containing anions. Fig. 13 shows the temperature dependence of the susceptibility of κ - $(\text{BETS})_2\text{FeBr}_4$ measured on a sample composed of crystals oriented with their plate plane parallel to each other. Both susceptibilities measured with the field parallel or perpendicular to this plane are well described by the Curie–Weiss law [$\chi = C/(T - \theta)$] in the 100–300 K temperature range with $\theta = -5.5$ K. The $C = 4.70$ K emu mol⁻¹ value indicates a high spin-state for the Fe^{3+} ions (compare with the 4.38 K emu mol⁻¹ value calculated [$N_A g^2 m_B S(S + 1)$] for a $S = 5/2$ localised spin system with $g = 2.0$). The large anisotropy below 2.5 K indicates an AF ordering of the Fe^{3+} spins. A recent re-examination of the susceptibility by using one single crystal confirms a standard AF behaviour with the easy axis parallel to the a axis. To our knowledge, κ - $(\text{BETS})_2\text{FeBr}_4$ seems to be the first molecule-based conductor with an AF metal state at ambient pressure.

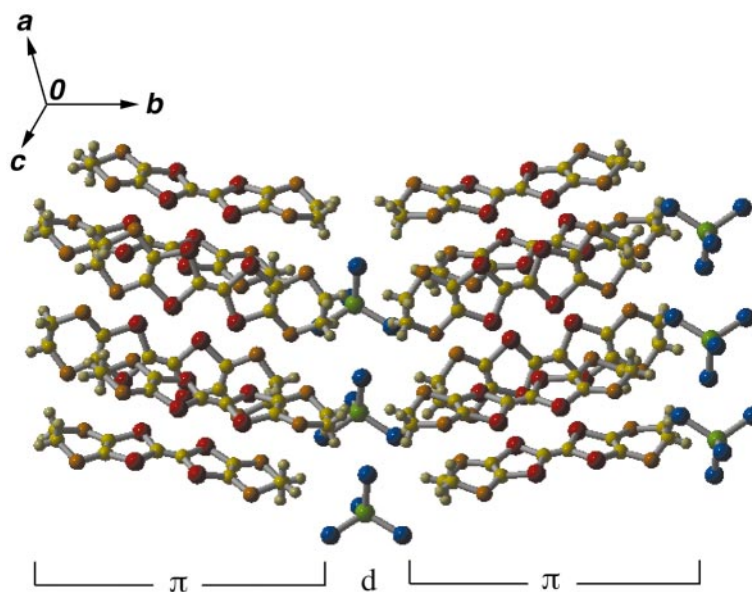


Fig. 11 Crystal structure of κ - $(\text{BETS})_2\text{FeBr}_4$. Cl atoms, blue; Fe, green; Se, red; S, brown; C, yellowish green.

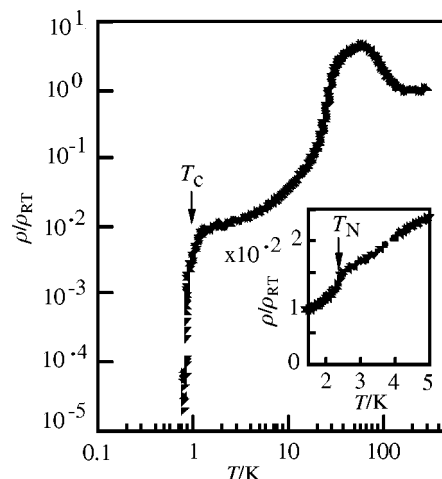


Fig. 12 Temperature dependence of the resistivity of κ - $(\text{BETS})_2\text{FeBr}_4$. The insert shows the resistivity drop at the AF transition temperature.³³

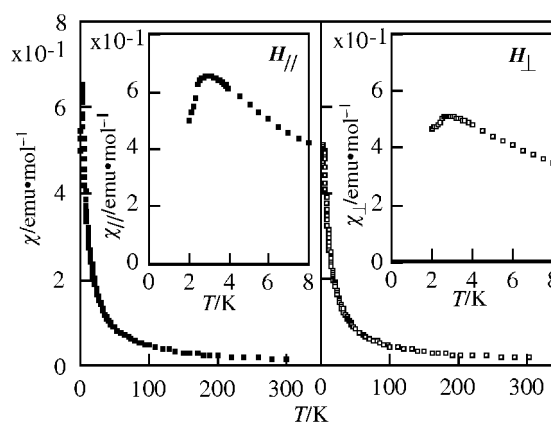


Fig. 13 Magnetic susceptibilities of plate-shaped crystals of κ - $(\text{BETS})_2\text{FeBr}_4$ for the field applied parallel (H_{\parallel}) and perpendicular (H_{\perp}) to the crystals plane (redrawn after ref. 33).

Around 2.5 K ($\approx T_N$; see Fig. 12), the resistivity of κ - $(\text{BETS})_2\text{FeBr}_4$ exhibits a small drop which emphasises, for the first time in the case of molecular conductors, the importance of the π -d interaction. Furthermore, this compound undergoes a SC transition below 1.3 K (T_c (midpoint) = 1.1 K). Resistivity measurements under magnetic field show that the critical field parallel to the conduction plane is one order of magnitude larger

than that perpendicular to it. The coherent length is roughly estimated about 350 Å and 35 Å along the parallel and perpendicular directions, respectively.³⁵ The specific heat measured by thermal relaxation method shows a λ -type peak at 2.4 K that corresponds to the Neel temperature obtained by magnetic measurements. The calculated entropy reaches the expected value $R \ln 6$ around 3.8 K, which corresponds to the full spin freedom of Fe^{3+} spins ($R \ln(2S + 1)$ with $S = 5/2$). Moreover, no anomaly was detected at 1.1 K, showing that the AF order of Fe^{3+} spin system is not destroyed by the onset of the superconductivity.³⁵ This means that magnetic order and superconductivity coexists below T_c . Thus, κ -(BETS)₂FeBr₄ may be also considered as the first magnetic molecular superconductor.

Since the shortest Fe...Fe distance is rather long (> 5.9 Å), the weak direct dipole–dipole interaction cannot be accounted for explaining the magnetic interaction. Considering that BETS layers along the b -direction separate the anions, the magnetic interaction mediated by the BETS molecules must be essential for establishing a three-dimensional magnetic order. Very recently, we have observed in κ -(BETS)₂FeCl₄ AF and SC transitions whose T_N and T_c are lower than those of κ -(BETS)₂FeBr₄.³⁶ Given the smaller unit cell of κ -(BETS)₂FeCl₄ compared to that of κ -(BETS)₂FeBr₄, the lower T_N of κ -(BETS)₂FeCl₄ further supports the idea that the Fe...Fe magnetic interaction is mediated by the BETS molecules. Thus, the π electron structure of the BETS molecule seems to be responsible for both superconducting and AF interactions below T_c . The full elucidation of the mechanism of the magnetic and superconducting interactions in κ -(BETS)₂FeX₄ ($X = \text{Cl}, \text{Br}$) remains an exciting challenge.

8 Conclusions

At the beginning of 1990s, when the molecular design of the molecular conductors having stable π metal states seemed to be almost routine, there was no example of magnetic molecular conductors in which π metal-like conduction electrons and magnetic moments incorporated in the crystals coexisted at low temperature. By using 2- D , BETS salts incorporating magnetic anions with large magnetic moments, various types of new magnetic conductors have been discovered, including the first molecular AF metal, λ -(BETS)₂FeCl₄, the first conductor with an AF metal state at ambient pressure, κ -(BETS)₂FeBr₄. Moreover, one of the final targets in the development of magnetic molecular conductors, *i.e.*, an AF superconductor, has been reached through the characterisation of this very same κ -(BETS)₂FeBr₄ compound. Lastly, conductors exhibiting unprecedented superconductor–insulator and superconductor–metal transitions have been observed in the λ -(BETS)₂Fe_xGa_{1-x}Cl_{4-y}Br_y series.

These results were obtained to our surprise, in spite of the very simple design strategy and in spite of the rather simple crystal structures of the BETS-based conductors. At first, one would have expected the π - d interaction in these types of conductors to be very small because the magnetic anions are distinctly separated from the conduction layers of the donor molecules. Nevertheless, the λ -(BETS)₂FeCl₄ and κ -(BETS)₂FeBr₄ conductors exhibit magnetic transitions at fairly high temperatures. Furthermore, the direct evidence of an interaction between π metal electrons and magnetic moments localised on the anions was observed in the resistivity behaviour around the Neel temperature of κ -(BETS)₂FeBr₄.

One of the next goals in the development of new molecular conductors may be the realisation of a pure molecular ferromagnetic metal whose spin origin would be an organic radical. Indeed, one drawback of the purely organic molecule-based ferromagnets developed so far is that the ferromagnetic

interaction in these systems is rather weak. It could be possible that such interaction would be much enhanced if conduction electrons mediate it.

Based on the results of the recent development of magnetic molecular conductors reviewed in the present work, it appears that the ability of molecule-based materials to afford new systems with unprecedented electronic properties seems to be surprisingly high. This is a strong incentive for a further development of molecular systems with novel electronic functions.

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