Molecular Spin Ladders

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Abstract: The structural and magnetic characteristics of the recently discovered quantum spin ladders are summarised and the possibilities of supramolecular chemistry for developing such fascinating materials are discussed. The existing examples of molecular spin ladders clearly show that typical supramolecular and crystal engineering criteria, such as $\pi-\pi$ overlap, $S\cdots S$ and $C{-}H\cdots S$ interactions and complementarity of size and shape, are useful in the construction of these magnetic quantum systems with intermediate dimensionalities between one-dimensional chains and two-dimensional square lattices.

Keywords: crystal engineering · molecular magnetism · molecular materials · radical ions · spin ladders

What Is a Spin Ladder?

Spin ladders are low-dimensional magnetic quantum systems that consist of a finite number of strongly magnetically coupled chains of spins that are at the crossroads between one and two dimensions (Figure 1). Especially interesting are the ladders with $S = 1/2$ spins, which show antiferromagnetic isotropic coupling between the nearest neighbours, and that are generally named as $S = 1/2$ Heisenberg antiferromagnetic spin ladders. The Hamiltonian in Equation (1), defines such magnetic systems. In Equation (1) $S_{i,a}$ is the spin operator at the site i ($i = 1,2,\ldots,L$) on the leg a ($a = 1,2\ldots$) of a ladder with L rungs. $J_{\perp}$ and $J_{\parallel}$ denote the intra- and inter-rung exchange coupling respectively. With this definition, $J_{\perp}$ and $J_{\parallel}$ should be positive for antiferromagnetic interactions.

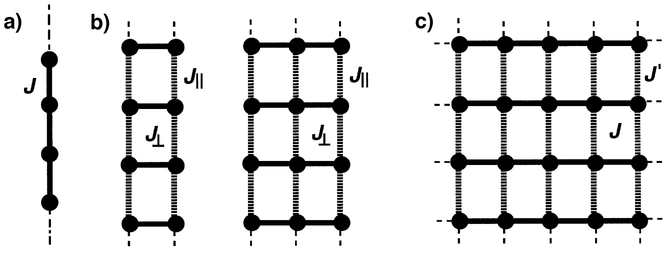

Figure 1. Schematic illustration of different kinds of low dimensional magnetic Heisenberg systems with antiferromagnetic couplings: a) one-dimensional chain; b) two- and three-leg spin ladders in which $J_{\perp}$ is the coupling along the rungs and $J_{\parallel}$ is the coupling along the chains; c) two-dimensional square lattice with different exchange coupling constants, J and J'. Black dots denote $S = 1/2$ spin-containing units and continuous and dashed lines represent antiferromagnetic interactions of different strength.

$$H = J_{\parallel}\sum_{a=1}\sum_{i=1}^{L} S_{i,a}S_{i+1,a} + J_{\perp}\sum_{i=1}^{L} S_{i,1}S_{i,2} \qquad (1)$$

The magnetic properties of such systems are particularly interesting as a result of the increased importance of the quantum-mechanical effects operating within them. Theoretical calculations have predicted that spin ladders with an even number of legs have a spin-liquid ground state, so called because of their purely short-range spin correlation along the legs. These even-leg ladders consist of spin singlet pairs with a spin–spin correlation distance along the legs that show an exponential decay produced by the presence of a finite spin gap. By contrast, a ladder with an odd number of legs behaves quite differently and displays properties similar to those of a one-dimensional antiferromagnetic Heisenberg chain at a low thermal energy, namely, gapless spin excitations and a power-law falloff of the spin–spin correlations which are magnetically ordered.[1–9]

Magnetic properties of two-leg $S = 1/2$ antiferromagnetic spin ladders can be easily described for the case in which intra-rung exchange coupling is much larger than the exchange coupling along the legs; $J_{\perp} \gg J_{\parallel}$. In this particular case the rungs of the ladder interact only weakly with each other and the dominant spin configuration in the ground state is that with the spins on each rung forming a spin singlet. Therefore, the ground state has a total spin $S = 0$. To produce the lowest excitation in the infinite ladder to a configuration with a total spin $S = 1$, one of the rung singlets of the ladder must be promoted to an $S = 1$ triplet (Figure 2) with a finite energy that must overcome the finite spin gap of the system. Moreover, the coupling along the legs creates an energy band of $S = 1$ magnons with a dispersion of about $2J_{\parallel}$ that leads to an exponential decrease in the magnetic spin susceptibility as the temperature is lowered until kT is below the spin-gap energy.

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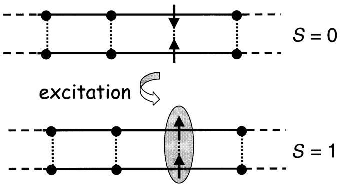


Figure 2. Schematic illustration of the lowest excitation to a configuration with a total spin $S = 1$ in a two-leg $S = ½$ Heisenberg antiferromagnetic ladder with $J_{\perp} > J_{\parallel}$.

Another interesting prediction for two-leg ladders is that light hole-doping can lead to superconductivity on basis that effective attraction between extra holes may arise from the magnetic interactions between the spins of the ladders.[2] Odd-leg ladders, on the other hand, must have different behaviour because singlet pair formation on their rungs is not possible.[4]

"Ideal" spin ladders are those in which the exchange coupling along the rungs is very similar to the exchange coupling along the chains, that is $J_{\perp}/J_{\parallel} \approx 1$. Therefore such systems are intermediate between two limiting cases: a) isolated dimers, when $J_{\perp}/J_{\parallel} \rightarrow \infty$, and b) isolated one-dimensional chains, when $J_{\perp}/J_{\parallel} \rightarrow 0$. Spin ladders of experimental interest are those that have both exchange coupling constants of the same order of magnitude, that is $0.1 \leq J_{\perp}/J_{\parallel} \leq 10$. In addition, ladders should be quite well isolated one from another, since appreciable interladder coupling (J' in Figure 3) can promote a quantum phase transition between the spin-liquid ground state and a magnetically ordered state. Troyer et al. established a critical ratio of the interladder to intraladder coupling of $J'/J_{\perp} \approx 0.1$ that separates the spin liquid from an antiferromagnetic-ordered state.[10]

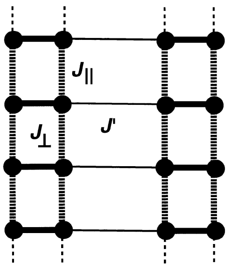


Figure 3. Scheme of two-leg ladders showing intraladder ($J_{\perp}$ and $J_{\parallel}$) and interladder (J') exchange couplings. Black dots denote $S = ½$ spin-containing units.

The appealing properties of spin ladders have been only recently found in very few materials, the first examples being connected chains of transition metals in inorganic oxides, such as the series of even- and odd-leg ladder structures provided by the cuprates $Sr_{n-1}Cu_{n+1}O_{2n}$ ($n = 3, 5, \ldots$),[11] or the two-leg ladders $(VO)_2P_2O_7$[12] and $LaCuO_{2.5}$.[13] However, it is important to note that the identification of these compounds as spin ladders have been made, primarily, on the basis of their macroscopic characterisation (magnetic susceptibility data) and it has been shown later on that microscopic probes, such as neutron scattering, nuclear magnetic resonance (NMR) and muon spin resonance (μSR), are necessary to establish the exact nature of the ground state. In fact, although the family of cuprates containing Sr has been confirmed as real spin ladders by different experiments,[14] NMR and μSR studies on the La-containing cuprate[15, 16] and inelastic neutron scattering measurements on the $(VO)_2P_2O_7$[17] showed that both of these compounds are not real spin ladders.

Abstract in Catalan: *En aquest article es descriuen les característiques estructurals i magnètiques de les escales de espí, sistemes quàntics recentment descoverts, i es discuteixen les possibilitats que ofereix la química supramolecular per tal de desenvolupar aquests materials fascinadors. De fet, els exemples que existeixen de escales de espí moleculars ens mostren clarament que els criteris utilitzats habitualment en enginyeria cristal · lina i supramolecular com son el solapament d'orbitals π, les interaccions S ⋯ S i C–H ⋯ S i la complementarietat de forma i grandària són també eines de gran utilitat a l'hora de construir aquests sistemes magnètics quàntics que tenen una dimensionalitat intermèdia entre les cadenes 1D i les xarxes 2D.*

The search for new compounds that have spin-ladder properties is a very important task not only for understanding the fascinating quantum ladder physics, but also for developing new materials, especially superconductors.

The First Molecular Spin Ladders

Nowadays, from the viewpoint of chemists in the field of molecular materials science, one of the most exciting topics is solid-state supramolecular synthesis, that is, to combine appropriate molecular building blocks in a predesigned way as to endow the resulting supramolecular assembly with desirable physical properties. Because of their structural flexibility, molecular solids offer a field of choice to finely tune interesting physical properties such as those of the spin-ladder materials. In fact, in materials constructed from open-shell molecules, the modulation of their structural, electronic and magnetic dimensionalities has permitted the realisation of molecular compounds that have a large variety of physical phenomena ranging from low-dimensional metals and superconductors to organic ferromagnets.[18, 19] The main interest of these new materials arises from the fact that the interacting spins are located in molecular orbitals (MO) with a large or dominant role of s and p atomic orbitals rather than of d and f orbitals as in ordinary metals and magnets. Moreover, the modulation of their crystal structures and thereby of their electronic and magnetic dimensionalities can be achieved by modifying the type and/or the strength of intermolecular interactions present in the crystal. By changing the structure and components of the molecular units, such modification can, in principle, be accomplished.

The construction of the simplest molecular spin ladder—a two-leg ladder—can be conceptually achieved following two different strategies (Figure 4). The first one consists of the connection of two molecular one-dimensional $S = ½$ spin chains, one next to the other. The second strategy is to assemble an infinite number of units with two interacting $S = ½$ molecules (dimers). Consequently, the selection of the appropriate open-shell building blocks, able to form one-dimensional chains or dimers and that are also able to interact with the neighbouring units, is of primary importance. Although the few molecular spin ladders known so far have been obtained by serendipity, the study of these compounds

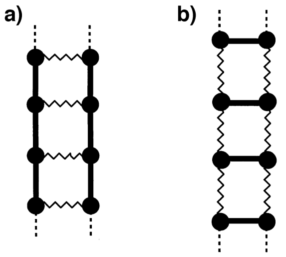


Figure 4. Illustration of the two strategies that can be used in the construction of molecular two-leg ladders: a) assembly of one-dimensional $S = ½$ chains and b) connection of $S = ½$ dimers.

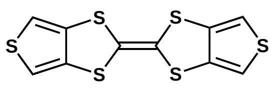
shows that both conceptual strategies have been involved in their construction.[20–23]

To follow the first strategy—the assembly of chains—one of the most promising building blocks are tetrathiafulvalene (TTF) derivatives, since it is well known that these planar π-electron donors form stable radical cations that have a large tendency to stack forming one-dimensional chains.[18, 19] Furthermore, the transfer integral (t) between electrons in neighbouring molecules are comparable or even smaller than the on-site Coulombic repulsion (U), and thus the electron wave function is very often on the borderline between the localised and delocalised behaviour. When localisation of the electrons is promoted, by lowering the t/U ratio, a one-dimensional spin chain can be generated that could provide the legs of the ladders if interchain magnetic interactions are adequate. In fact the sulfur atoms of TTF derivatives readily establish intercolumn structural and electronic interactions, thus promoting enhanced electronic dimensionality in a great number of metallic charge-transfer salts derived from these mainly planar molecules.[24] Therefore, S ⋯ S interactions could provide the rungs of the ladder. Exchange coupling constants, J_i, among open-shell molecules in these TTF-based molecular spin ladders are related to the transfer integral, t_i, of the corresponding intermolecular contact and the on-site Coulombic repulsion, U, of the molecule by Equations (2).

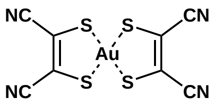
$$J_i = 2t_i^2/U \qquad (2)$$

Due to the above mentioned characteristics one-dimensional and two-dimensional, layered organic conductors based on TTF are quite common in the literature[18, 19] although the achievement of an intermediate dimensionality, that is, a finite number of assembled stacks forming ladder-like structures, have been only recently accomplished.[20, 21] Only when the proper array of diamagnetic counterions cuts a two-dimensional-layered TTF structure with localised electrons is a spin-ladder molecular material obtained in the donor sublattice.

Our research group have succeeded in preparing a purely organic molecular two-leg spin-ladder compound using as a building block the TTF derivative dithiophenetetrathiafulvalene (DT-TTF) and the Au complex of the maleonitrile dithiolate $[Au(mnt)_2]^-$as a counterion.[20] This planar diamagnetic counterion has the same size as the donor and also exhibits a great tendency to stack forming one-dimensional chains; it therefore complements DT-TTF.



DT-TTF



$[Au(mnt)_2]$

The molecules crystallise together to form the mixed-valence salt $[(DT\text{-}TTF)_2][Au(mnt)_2]$, in which segregated DT-TTF and $[Au(mnt)_2]$ stacks with a herringbone pattern are present (Figure 5). At room temperature, the DT-TTF stacks are arranged in pairs, related by a twofold screw axis, that alternate with single stacks of $[Au(mnt)_2]$ units along the $a - c$ direction. The pairs of organic donor stacks are the legs of a two-leg ladder structure, since they are strongly linked by three inter-stack S ⋯ S close contacts (Figure 5b), providing the rungs for the ladder. In fact the calculated transfer integrals show that the two legs of the ladder interact strongly, since the value of the transfer integral coupling the two paired chains of donors ($t_{\perp} = 21$ meV) is very similar to that of the transfer integral up the chain ($t_{\parallel} = 36$ meV).

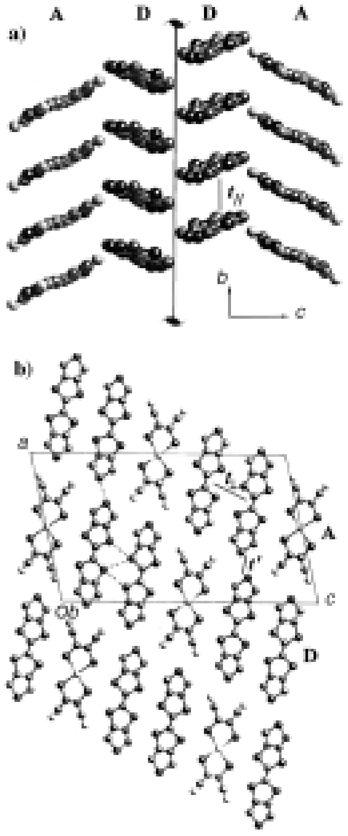


Figure 5. a) Crystal packing of $[(DT\text{-}TTF)_2][Au(mnt)_2]$ showing the ladder structure formed by the organic DT-TTF donor (D) stacks related by a two-fold screw axis ($A = [Au(mnt)_2]$); b) projection of the crystal structure along the b axis, in which short S ⋯ S contacts are indicated by dotted lines.

The structural arrangement of donors in $[(DT\text{-}TTF)_2][Au(mnt)_2]$ is the same as that found in the two-dimensional organisation of the neutral donor in the solid state;[25] therefore, the structure of this salt can be described by separating, in pairs of stacks, the two-dimensional arrangement of the neutral DT-TTF with the stacks of anions. By using a diamagnetic anion of similar size and shape to that of the donor molecules, we have succeeded in the realisation of an intermediate dimensionality between one and two dimensions for a molecular compound. This structural ladder should have localised, interacting electrons in order to behave as a two-leg spin ladder; otherwise it could behave as a one-dimensional metal. Indeed, electrical-transport measurements and X-ray diffuse scattering experiments show that below 220 K the electrons are localised in dimers of DT-TTF molecules (Figure 6). These dimers $[(\text{DT-TTF})_2]^{\bullet+}$ constitute the spin-carrying units of the spin ladder.

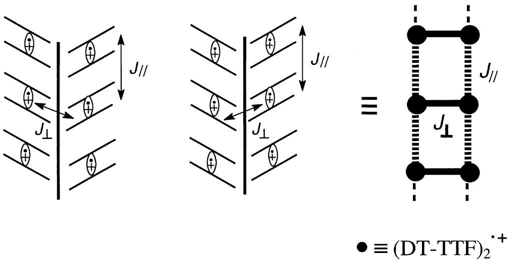


Figure 6. Schematic illustration of the two possible two-leg ladders formed by the dimerisation of DT-TTF stacks in $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$.

Susceptibility data on powdered and single-crystal samples of the salt show a characteristic behaviour of localised spins with strong antiferromagnetic interactions, which display a spin gap (Figure 7). The exponential decay of susceptibility data at low temperature (from 8 to 45 K) were successfully fitted with the Troyer expression [Eq. (3)][7] for a two-leg spin-ladder system with the energy gap, Δ/k, in the spin excitation spectrum found to be equal to 78 K.

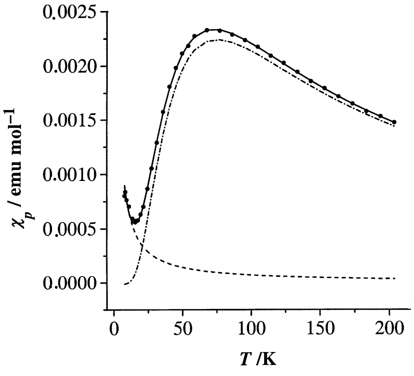


Figure 7. Temperature dependence of the paramagnetic susceptibility (•) of the $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$ salt. The solid line is the fit by Equation (2) to a contribution of a spin-ladder model (•–•–) and a Curie tail (- - - -).

$$\chi_{\text{ladder}} = \alpha T^{-1/2} \exp(-\Delta/kT) \tag{3}$$

The exchange interactions along the legs ($J_\parallel/k = 83$ K) and the rungs ($J_\perp/k = 142$ K) of the ladder were extracted by fitting of the whole susceptibility data with the Equation (4), which takes into account the Curie contribution due to paramagnetic impurities (defects) in the crystals. The two-leg ladder model Equation (5) used for such a fitting was that developed by Barnes and Riera, in which c_1, c_2, c_3, c_4, c_5 and c_6 depend on $J_\perp$ and $J_\parallel$ (Figure 7).[12b]

$$\chi = f\chi_{\text{ladder}} + (1-f)\chi_{\text{Curie}} \tag{4}$$

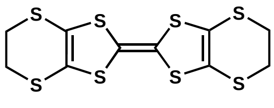
$$\chi_{\text{ladder}}(T) = \frac{c_1}{T}\left[1 + \left(\frac{T}{c_2}\right)^{c_3}(e^{c_4/T} - 1)\right]^{-1}\left[1 + \left(\frac{c_5}{T}\right)^{c_6}\right]^{-1} \tag{5}$$

Of note for this two-leg spin ladder is the fact that the $J_\perp/J_\parallel$ ratio is 1.7, which is close to that of an ideal spin ladder. The spin gap has also been calculated from the resulting values of $J_\parallel$ and $J_\perp$ with the theoretical Equation (6)[7] to give $\Delta/k =$ 83 K, which is in good agreement with the previous value.

$$\Delta = J_\perp - J_\parallel + J_\parallel^2/2J_\perp \tag{6}$$

The temperature dependence of the magnetic susceptibility clearly inferred that the $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$ salt is a purely organic molecular system with a two-leg spin-ladder configuration. Nevertheless, since the calculated interladder transfer integral $t' = 6$ meV, although small, is not negligible and could imply a quite sizeable ladder–ladder interaction (J') that affects the nature of the low-temperature magnetic state, independent magnetic measurements were performed. Zero field and longitudinal field μ^+SR measurements as a function of temperature have confirmed that $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$ is a molecular material with a real two-leg spin-ladder configuration, since the results obtained corroborate the absence of a magnetic ordering, as expected for even-leg spin ladders with the quantum spin-liquid state realised.[26]

Another TTF based organic spin ladder has been claimed by Komatsu et al.[21] The compound belongs to the fruitful family of bis(ethylenedithio)tetrathiofulvalene (BEDT-TTF)



BEDT-TTF

salts. Its structure consists of two uniform stacks of completely ionised BEDT-TTF donors along the c axis that are isolated from the neighbouring pairs of stacks by the diamagnetic $[\text{Zn(SCN)}_3]^-$anions as shown in Figure 8. The $[\text{BEDT-TTF}]^{\bullet+}$ stacks form a structural two-leg ladder, since they are connected by side-by-side S⋯S interactions (interaction labelled as 3 in Figure 8) between BEDT-TTF molecules as well as by another weaker face-to-face interactions (interaction labelled as 2 in Figure 8).

The low conductivity and the semiconducting behaviour of this salt denote that electrons are localised in the BEDT-TTF molecules. Based on the calculated transfer integrals, the authors argue that there are four possible exchange coupling constants: one intrachain ($J_1/k = 966$ K), two interchains ($J_2/k = 5.2$ K and $J_3/k = 86.4$ K) and another ($J_4/k_B = 0.09$ K) with an interladder character. Nevertheless, only two of these magnetic couplings ($J_1 \equiv J_\parallel$ and $J_3 \equiv J_\perp$) can be considered as effective (Figure 9).

The fit of the experimental susceptibility data (Figure 10) to the spin-ladder model [Eq. (3)] gives an energy gap of 340 K. Nevertheless, in this case the energy gap calculated from the $J_\parallel$ and $J_\perp$ values, estimated from the transfer integrals, shows a

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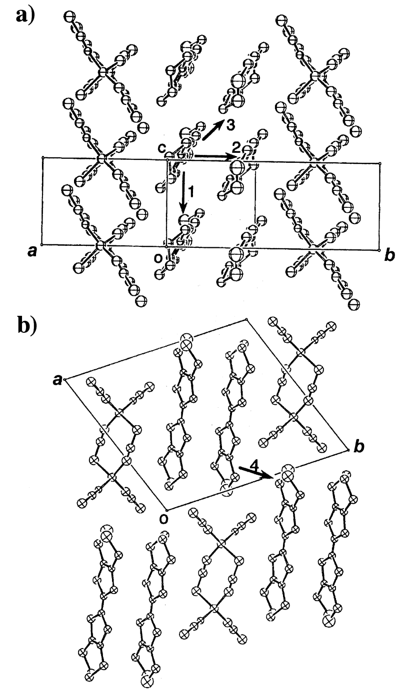


Figure 8. X-ray structure of [BEDT-TTF][Zn(SCN)$_3$] by Komatsu et al.[21] a) View along the molecular long axis of BEDT-TTF; b) view along the *c* axis. Arrows indicate the interactions within (interactions 1–3) and between (interaction 4) the ladder. (Reprinted with permission.[21])

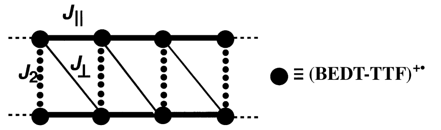


Figure 9. Schematic representation of the two-leg spin ladder formed by the two chains of [BEDT-TTF]$^{\bullet+}$ in [BEDT-TTF][Zn(SCN)$_3$].

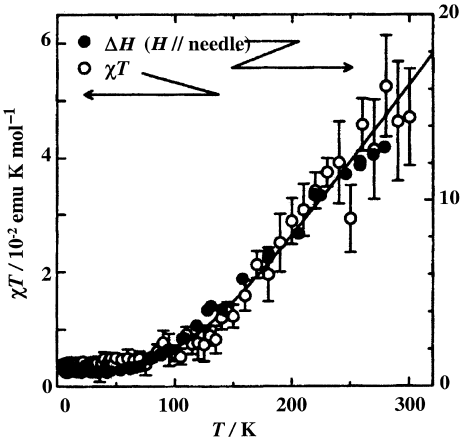
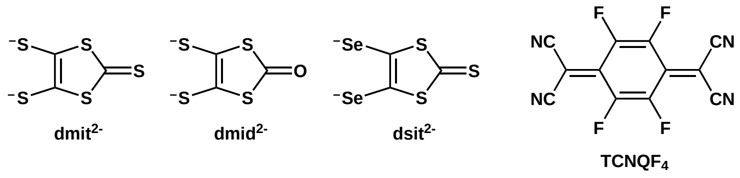


Figure 10. Plot of χT vs. T for the [BEDT-TTF][Zn(SCN)$_3$] salt (open circles). The solid line is the best fitting curve to the spin-ladder model [Eq. (3)]. Temperature dependence of ESR line-width (closed circles) of an oriented single crystal is also shown. (Reprinted with permission.[21])

large discrepancy with the experimental ones. The authors stated that this result could probably be accounted for by the frustrating effect of the antiferromagnetic interaction J_2 (Figure 9). Finally, it must be pointed out that the $J_\perp/J_\parallel$ ratio of 0.1, estimated from the transfer integrals, place this two-leg spin ladder at the limit in which it could also be described as pairs of weakly interacting one-dimensional chains.

The second strategy to the two-leg ladder systems—the assembly of an infinite number of dimers—has been also successful in the achievement of molecular spin ladders. In all known cases the spin-carrying units are not purely organic, but are metal dithiolene complexes.

Fourmigué et al.[22] have found spin-ladder properties in some members of a family of charge-transfer complexes formed by tetrafluorotetracyanoquinodimethane (TCNQF$_4$) and cyclopentadienyl/dithiolene (dithiolene = dmit^{2-}, dmid^{2-}, dsit^{2-}) Mo and W complexes.



The strong electron-acceptor TCNQF$_4$ oxidises the organometallic donors that are organised in the solid as head-to-tail dimers. Since TCNQF$_4$$^{\bullet-}$radical anions are strongly dimerised into diamagnetic [TCNQF$_4$]$_2$$^{2-}$species, only the [Cp$_2$M(dithiolene)]$^{\bullet+}$ radical cations are responsible for the magnetic properties shown by these solids. The reported [Cp$_2$M(dmid)][TCNQF$_4$] (M = Mo, W) complexes are isostructural being the [Cp$_2$M(dmid)]$^{\bullet+}$ radical cations dimerised by dmid/dmid π–π overlap interactions. Such dimers constitute the rungs of the ladder, since they are strongly interacting owing to short S$\cdots$S contacts, this gives rise to ladder-type structures that are isolated from each other by the chains of TCNQF$_4$ (Figure 11).

Accordingly with the described structural characteristics, the exponential decay of susceptibility data below the maximum can be fitted to the Troyer equation [Eq. (1)] giving different spin gaps for both compounds (Figure 12): $\Delta/k = 74$ K and $\Delta/k = 13$ K for the Mo and W salts, respectively. Thus, the replacement of W for Mo, while not altering the structural characteristics of the supramolecular structures, modifies the electronic characteristics of the building block and as a consequence the electronic structure of the molecular spin ladder.

The authors extracted the values of $J_\parallel$ and $J_\perp$ combining the Equations (6) and (7). The obtained exchange coupling constants for the Mo salt were $J_\perp = 107$ K and $J_\parallel = 41$ K and for the W salt $J_\perp = 23$ K and $J_\parallel = 16$ K. The relative values of these constants are in accordance with the smaller dithiolene contribution to the SOMO for the W complex and are also in very good agreement with the calculated interaction energies within the dimers. Remarkable also are the $J_\perp/J_\parallel$ ratios of 2.6 and 1.5 for Mo and W salts, respectively, since they are close to that of an ideal two-leg spin ladder.

$$T(\chi_{\max})/J_\perp = 0.625 - 0.01835\,J_\parallel/J_\perp + 0.2532\,(J_\parallel/J_\perp)^2 \qquad (7)$$

The complex [Cp$_2$W(dmit)][TCNQF$_4$] also presents interacting dimers although with another type of dimer association, due to S$\cdots$S interactions instead of π–π overlap. The

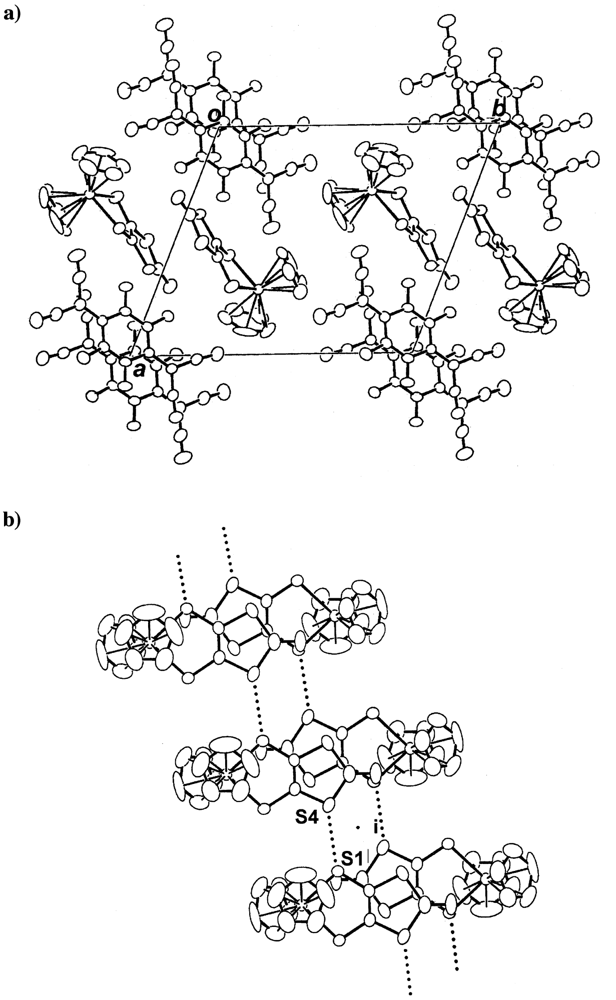


Figure 11. a) X-ray structure of $[Cp_2Mo(dmid)][TCNQF_4]$ by Fourmigué et al.[22] b) View of the ladder structure formed by the $S = ½$ cations in the $[Cp_2Mo(dmid)][TCNQF_4]$ salt.

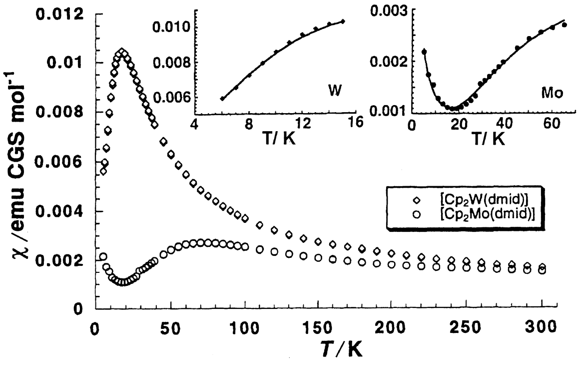
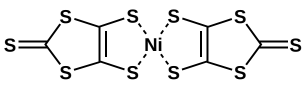


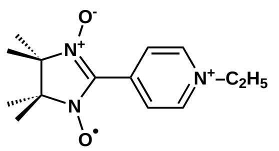
Figure 12. Plot of magnetic susceptibility vs. T of the $[Cp_2M(dmid)][TCNQF_4]$ (M = W, Mo). Insets show the fits of the low-temperature data to [Eq. (3)].[22]

susceptibility data was analysed as in the other complexes giving a spin gap value of $\Delta/k = 40$ K.[22]

The last known example of molecular spin ladder is provided by another dithiolene complex, the π-radical anion $[Ni(dmit)_2]^{\bullet -}$.[23] This $S = ½$ ion also forms dimeric units that interact in a ladder-like structure in the salt formed with a paramagnetic counterion, the p-N-ethylpyridinium α-nitronyl nitroxyde ([p-EPYNN]).



$[Ni(dmit)_2]$



p-EPYNN

In the crystal structure of $[p\text{-EPYNN}][Ni(dmit)_2]$ salt, the open-shell p-EPYNN cations form chains along c axis that isolate the chains of dimers, formed also along c axis, by the dithiolate radical anions (Figure 13). The dimers of $[Ni(dmit)_2]^{\bullet -}$are formed by a π–π overlap and the connection between the dimers are provided by very short (3.31 Å) S···S contacts that take place along the c axis.

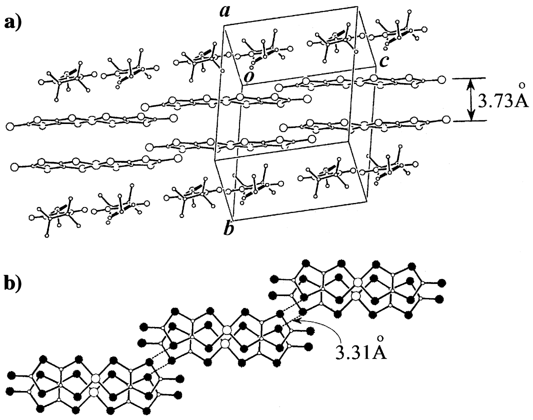


Figure 13. Crystal structure of $[p\text{-EPYNN}][Ni(dmit)_2]$ salt by Imai et al.[23] a) Both chains of cations and anions are shown. b) View of $[Ni(dmit)_2]$ ladder showing the short S···S interdimer contacts. (Reprinted with permission.[23])

In contrast to the previous $[Cp_2M(dithiolene)][TCNQF_4]$ compounds, the crystals of $[p\text{-EPYNN}][Ni(dmit)_2]$ contain two different magnetic subsystems: the p-EPYNN radical cation chains and the one-dimensional ladder chain of $[Ni(dmit)_2]^{\bullet -}$radical anions. On the basis of macroscopic magnetic investigations, the authors ascribe a spin ladder behaviour for the chain of dimers formed by the $[Ni(dmit)_2]$ radical anions and a ferromagnetic chain behaviour for the p-EPYNN radical cation chains, stating that both subsystems behave independently. The fitting of the susceptibility data shown in Figure 14 to the sum of expressions for a spin ladder [Eq. (3)] and for a one-dimensional chain with ferrromagnetic coupling[19d] gave a spin gap $\Delta/k = 940$ K for the $[Ni(dmit)_2]$ ladder and a ferromagnetic exchange interaction of $J/k = -0.16$ K for the [p-EPYNN] chains. Unfortunately, the authors have not determined the $J_\perp$ and $J_\parallel$ values of their system although from the resulting large spin gap value one expects a tiny $J_\perp/J_\parallel$ ratio for the spin ladder, well above the value for an ideal spin ladder.

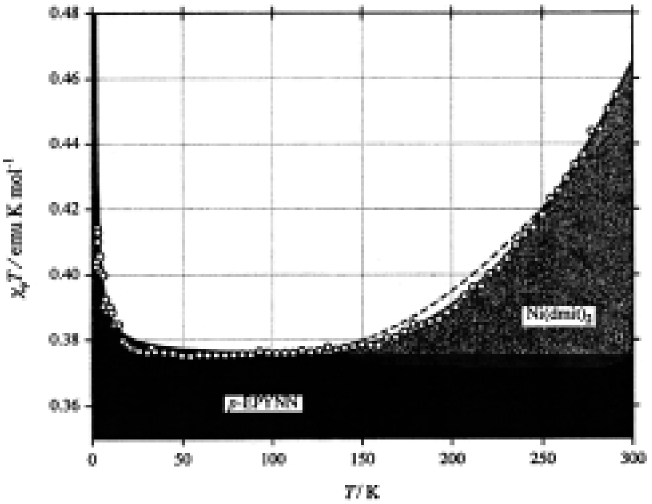


Figure 14. Plot of susceptibility of [p-EPYNN][Ni(dmit)$_2$] vs. T.[23] The solid curve is the fit to the sum of ladder and ferromagnetic chain equations and the black and grey regions represents the contribution from [p-EPYNN] and [Ni(dmit)$_2$], respectively. The broken curve is the best fit using a simple dimer model.

Challenges and Prospects

Although spin-ladder physics has emerged only very recently as a fertile subfield of condensed matter studies, molecular spin ladders have appeared at the initation of this area of research. In fact, the examples presented here show that supramolecular chemistry is a very powerful tool to construct solid compounds with tailored physical properties, such as spin ladders. Typical supramolecular and crystal-engineering criteria, like $\pi-\pi$ overlap, $S\cdots S$ interactions and complementarity of size and shape, used with success in the tuning of dimensionality and properties of molecular conductors and magnets have proven to be useful in the construction of intermediate magnetic dimensionalities which are the spin ladders. Although it is not an easy task, application of these criteria will help in increasing the number of examples of molecular spin ladders; this will in turn aid the understanding of low-dimensional spin systems that exhibit spin gaps. Important challenges in this field that deserve to be reached with molecular compounds are the construction of spin ladders with different values of ladder–ladder interactions and molecular spin ladders with more than two legs. Molecular compounds with such characteristics will help in the corroboration of theoretical findings about the limits of ladder–ladder exchange coupling interaction values that can destroy the ladder characteristics, as well as to verify the dependence of the bulk magnetic properties with the odd/even number of legs in the ladders.

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