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# Magnetism: Molecules to Build Solids

Michel Verdaguer<sup>\*[a]</sup> and Alain N. Gleizes<sup>[b]</sup>

**Abstract:** The seminal discovery in 1981 of bimetallic ferrimagnetic chains, based on the synthetic use of the concept “complex as ligand”, can be considered as a significant step on the way from molecules to more and more complex materials. We describe the chemistry, the structures, the magnetic properties of these 1D materials, together with the new theoretical models created to understand them. We then give an overview of some original creative ideas, which have irrigated the synthetic chem-

istry of brand-new molecular materials, room temperature magnets, photomagnetic and chiral magnets or functional surfaces. The review emphasizes that the celebrated individual “wins” are indeed the fruit, along the years, of the constructive multidisciplinary collaboration of many scientists, theoreticians and experimentalists, chemists and physicists. Difficulties, dead-end hypotheses, mistakes which represent a significant exciting part of any scientific endeavour, are not put under the rug.

## 1. Introduction


We were very surprised when we received the invitation to write a contribution for the Special Collection “Minireviews by Winners of the French Chemical Society Coordination Chemistry Division Prize”. For us, this “winning” distinction is far away (1984), we received since other distinctions supposed to be more prestigious and in any case, in our mind « Winner » for an individual scientist means nothing in science, which is a collective adventure where the individual endeavours blossom in a bath of many other contributions and, with a few exceptions,


are not possible without them. Furthermore, the well-known hazards of Prizes'attribution impede *a priori* to consider a “win” as an undisputable criterion of quality. Examples are available, not so far. Instead, the novelty, the creativity and the real impact that a seminal work can have on the future of the discipline are much more significant. We are not thinking of the disastrous h factor but of the eventual impulses given to a certain field by a nice result.

In our case, the Prize was shared by two scientists, Alain Gleizes (A. G.) and Michel Verdaguer (M. V). The work was undertaken in the frame of a collaboration between the team of Dr. Jean Galy at Laboratoire de Chimie de Coordination in Toulouse, where Alain was a researcher, and Prof. Olivier Kahn at Laboratoire de “Spectrochimie des Eléments de transition” at Orsay, our respective scientific supervisors. We are now Emeritus Professors respectively at Institut National Polytechnique de Toulouse where A. G. developed his scientific career as a crystal chemist and in the field of chemical vapour deposition (see section 8) and M. V. at Sorbonne Université in the field of molecular magnetism.

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Michel Verdaguer is Emeritus Professor at Sorbonne Université in Paris. He developed rational approaches to new molecular magnetic systems and to the use of synchrotron radiation. He is popularizing science with experiments. He holds Awards from the French and Royal Spanish Chemical Societies and from the French Academy of Sciences. He is a Fellow of Academia Europaea.



Alain N. Gleizes is Emeritus Professor at Institut National Polytechnique de Toulouse. His research activities concerned coordination chemistry (synthesis and crystallochemistry) and thin film materials grown by MOCVD. He developed collaboration with Russian and Romanian partners on educational (Dr.h.c. of the University of Pitesti) and research (University of Bucarest, Lomonosov University of Moscow, Nikolaiev Institute of Novosibirsk) programs.

## 2. A Novel Class of One-Dimensional Compounds

Our first common paper was entitled “*Ordered magnetic bimetallic chains: a novel class of one-dimensional compounds*”.<sup>[1]</sup> A. G. synthesized the compounds and solved the crystal structures in Toulouse. M. V. performed the magnetic measurements at Orsay on a Faraday balance, equipped with a helium cryostat. M. V. proposed an interpretation of the observed results. We decided to publish quickly, with the agreement of our supervisors and without them, an attempt to assert some scientific independence. Doing so quickly, we committed a mistake. The magnetic measurements revealed a deceiving non-magnetic ground state. They were performed carefully, but on a sample that had been modified during the measurements (see below). It took us two years to think about, to better understand the magnetism of ferrimagnetic chains, to overcome our mistake and to publish reliable data and more serious conclusions. Nevertheless, the original nature of our compounds, ordered bimetallic chains, the synthetic method (use of a metallic complex as building block), the brand new one-dimensional (1D) ferrimagnetism, a behaviour never tackled before by theoreticians, attracted enough attention to launch a new field of research on the way from molecules to magnets. One year later, the groups of Beltran and Drillon published an article on chains bound by EDTA, followed by a second paper bearing a title very similar to ours: “A new class of one-dimensional systems: the ordered bimetallic chains”.<sup>[2]</sup>

Some years later, O. Kahn wrote in his book:<sup>[3a]</sup> “The design of ferrimagnetic chains probably represents the most significant contribution of synthetic molecular chemistry to the area of magnetic materials”. Since, much water has passed under the bridges, and molecular magnetism has blossomed in many other ways. One of the aims of the present review is to critically examine this prodromo optimistic viewpoint.

## 3. Back to the Eighties: a “Winning” Convergence

At this time, most of the magnetic studies of molecular materials were related to the so-called magnetochemistry, where magnetic measurements, often at room temperature, were used to give more information on the structure of the complexes (octahedral, tetrahedral,...). Nevertheless, in different places, attempts were made to design new materials presenting significant physical properties (optical, conducting, magnetic ...). In the Laboratoire de Chimie de Coordination, created in 1974 in Toulouse, Galy, Gleizes, Cassoux were studying the structures of planar molecular blocks (such as  $[(O_2C_2S_2)Ni(S_2C_2O_2)]^{2-}$ , Nidto to check if they could give rise to conducting materials, when stacking.<sup>[5]</sup>

These endeavours were later developed by Cassoux and co-workers on molecular superconductors.<sup>[6]</sup>

In 1976, at Orsay, O. Kahn created the laboratory “Spectrochimie des Eléments de Transition” and gathered a few researchers in coordination chemistry, busy with spin cross-over systems, binuclear complexes, one-dimensional (1D) or two dimensional (2D) molecular materials. One of the main trends was

to use the theoretical model recently coined by O. Kahn and B. Briat further developed in ref.<sup>[3b]</sup> to create new compounds with new but foreseeable magnetic properties. *The dream and long-term goals were to transform molecules into magnets.* A nice scholarly account of this saga can be found in the book “Molecular Magnetism” published in 1993.<sup>[3]</sup> A more recent version can be found in ref.<sup>[4b]</sup>. M. V. and J.-J. Girerd at Orsay, were the “long chains” team. Among the homometallic chains, ferromagnetic ones were difficult to obtain and to crystallize (hence the use of EXAFS instead of X-ray diffraction), most of the chains were antiferromagnetic with a non-magnetic ground state.<sup>[7]</sup> Hence grew the idea to synthesize ordered heterometallic systems made of different spins to reach ferrimagnetism and long-range order. When the researchers in Toulouse explored the chemistry of Nidto, beyond the combination with alkali counterions<sup>[5]</sup> and used  $Zn^{2+}$  instead, they obtained the first bimetallic neutral chain built from the Nidto complex, chelating  $Zn^{2+}$ . « *Le composé mixte  $ZnNi(S_2C_2O_2)_2 \cdot 2.08H_2O$ , constitue, à notre connaissance, un premier exemple d'une chaîne unidimensionnelle à centres métalliques de natures diverses.* »<sup>[8]</sup> The compound presented a weak paramagnetism due to some octahedral paramagnetic  $Ni^{2+}$  ions distributed at random along the chain (4 %), when two water molecules coordinate to the otherwise square planar, diamagnetic,  $NiS_4$  unit. The following step was then obvious: replacing diamagnetic components by magnetic ones. The choice of  $[O_2C_2S_2CuS_2C_2O_2]^{2-}$ , Cudto, and  $Mn^{2+}$  was a way to reach the expected ordered magnetic object. This was achieved in 1980 by Gleizes.

## 4. Playing with Spins and Orbitals

The molecular magnetism scientist is playing with molecules and transition metals, with spins and orbitals. We love playing this game since the 80s. The first challenge is to find the way to organize electronic spins  $S_A$  and  $S_B$  on two sites A and B, either parallel or antiparallel. A convenient way to describe the spectroscopic levels of the system is to use the phenomenological spin Hamiltonian

$$\hat{H} = -J \cdot \hat{S}_A \hat{S}_B \quad (1)$$

where  $J$  is the coupling constant between the quantum spins.  $J$  can be of simple magnetic dipolar origin or controlled by exchange interaction. We are interested here mainly by the later. Several situations can arise, sketched in Figure 1. With two spins  $S = 1/2$  and  $J > 0$ , spins are parallel (Figure 1a), the ground state is a triplet,  $S_T = 1$ . The coupling, or interaction, is said ferromagnetic (F). When  $J < 0$ , the spins are antiparallel (Figure 1b), the ground state is a singlet,  $S_T = 0$ . The coupling is said antiferromagnetic (AF). A new situation arises when the two spins  $S_A$  and  $S_B$  are different ( $S_A > S_B$ ). The ferromagnetic case leads to the larger total spin ( $S_T = S_A + S_B$ ) whereas an antiferromagnetic interaction gives a smaller but non-zero spin ( $S_T = S_A - S_B$ ). The ground state is still magnetic. This situation is known as *ferrimagnetism*, first characterized in ferrites by Néel.<sup>[9]</sup>

The second challenge is to relate the coupling constant and its sign to the electronic structure of the compound (described by an orbital  $a$  on centre A and an orbital  $b$  on centre B). This

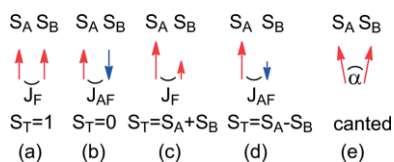


Figure 1. Playing with spins. Two spins  $S = 1/2$ : (a) parallel,  $S_T = 1$ ; (b) antiparallel  $S_T = 0$ . Two different spins: (c) ferromagnetically coupled, ( $S_T = S_A + S_B$ ); (d) antiferromagnetically coupled,  $S_T = S_A - S_B$ ; (e) canted spins.

is reminiscent of the situation of a weak bond between neighbouring centres and has been described either through the Hund-Mulliken approach by Hoffmann et al.<sup>[10]</sup> or through an Heitler-London scheme (Kahn, Briat).<sup>[3]</sup> For didactic summaries, see refs.<sup>[3,b]</sup>. To make a long story short, one can assert that, with the Kahn's model, applied to localized electrons, at the first order in  $S$ :

$$J = 2k + 4\beta S \quad (2)$$

where  $k$  is the exchange two-electrons integral between orbital  $a$  and orbital  $b$ ,  $\beta$  the resonance integral between  $a$  and  $b$  and  $S$  their overlap integral. The term  $2k$  is positive (resulting in a ferromagnetic contribution  $J_F$ ) and the term  $4\beta S$  is negative (resulting in an antiferromagnetic contribution  $J_{AF}$ ). A crude approximation leads to the conclusions that when the orbital overlap is zero (orthogonality), the coupling is ferromagnetic (Figure 1a), whereas when the overlap is non-zero,  $|4\beta S| > 2k$ , the coupling is antiferromagnetic (Figure 1b). In general,  $2k \ll |4\beta S|$  and  $J_F \ll |J_{AF}|$ . Overlap (and AF interaction) is the most common situation. "Le recouvrement est la chose du monde la mieux partagée". Orthogonality is more difficult to achieve and ferromagnetic interaction (F) case is rarer. When A and B present several  $n_A$  and  $n_B$  electrons in orbitals  $a_i$  and  $b_j$ , one takes into account the coupling constants  $J_{a,b}$  between orbitals  $a_i$  and  $b_j$

$$J = \frac{1}{n_A n_B} \sum_i \sum_j J_{a_i b_j} \quad (3)$$

In a one-dimensional (1D) infinite chain (Figure 2), the short-range interaction between neighbouring spins leads either to F chains (2a), AF chains (2b), alternating chains (2c) or ferrimagnetic chains (2d). The 1D world is a paradise for physicists and theoreticians since it allows to imagine, to write and sometimes to check a bunch of sophisticated Hamiltonians, to reach exact analytical solutions permitted by the reduced dimensions of the problem. Our 1981 paper, improved in 1984, reported the first ordered bimetallic ferrimagnetic chain, a model case never tackled before. The new compound needed new Hamiltonians,

## 5. Complexes Used as Ligands

The next – and essential – challenge for the chemist is to create the molecular system presenting the wanted structural, electronic and magnetic properties.

A 1D molecular chain is made by alternating transition metals A and molecular bridges M able to link A on both sides:  $-(A-M)_n$  ( $n$  infinite). When mixing  $M =$  oxalate anion  $(C_2O_4)^{2-}$ , well known to be bis-bidentate and  $A^{2+}$  ion =  $Cu^{2+}$ , one gets at

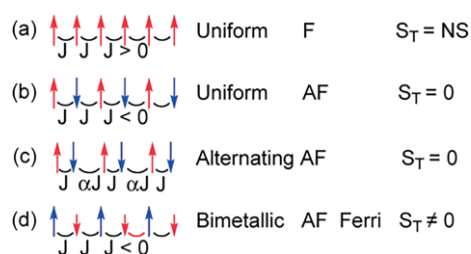


Figure 2. (a)  $J_F > 0$ , Uniform ferromagnetic chain. (b)  $J_{AF} < 0$ , uniform antiferromagnetic chain. (c) Chains with alternating  $J$  and  $\alpha J$ . (d)  $J_{AF} < 0$  between different spins, bimetallic ferrimagnetic chain.

once a nice light blue neutral chain  $-(CuC_2O_4)_n$ , CuOx. A similar chain  $-(B-M)_n$  is formed when mixing oxalate and metal  $B^{2+}$ ,  $-(Ni-C_2O_4)_n$ , NiOx, light green, for example. The constituents' ionic charges are crucial to get neutral repeating units along the chain and 1D entities or, instead, charged ones, when the chains must be separated by counterions, which is better to reveal the 1D behaviour, thanks to reduced inter-chains interactions  $J_{inter}$ .

To get an ordered bimetallic chain  $-(A-M-B-M)_n$ , as did the Toulouse's team in 1980<sup>[11]</sup> the synthetic chemist is faced to two major problems: (i) entropy which favours disorder in multi-components systems and (ii) kinetics of metal-ligand exchange. The solution implemented by Gleizes in ref.<sup>[11]</sup> relies on three synthetic rational "tricks": use of (i) a preformed molecular block  $(M-A-M)^{2-}$ , that is  $[(O_2C_2S_2)Cu(S_2C_2O_2)]^{2-}$  ( $[Cu(dto)_2]^{2-}$ ); (ii) a disymmetrical bis-chelating ligand, the dithio-oxalate anion  $(O_2C_2S_2)^{2-}$ ,  $(dto)^{2-}$ ; (iii) two metallic ions  $A^{2+} = Cu^{2+}$  and  $B^{2+} = Mn^{2+}$ , presenting different enough hard and soft acido-basic properties to bond preferentially to the two opposite sides of the ligand (that is, Cu to sulfur ends, Mn to oxygen), so that it is possible to achieve the crystallization of the ordered bimetallic neutral object:  $\{Mn^{2+}[(O_2C_2S_2)Cu(S_2C_2O_2)]^{2-}\}_n^0$  or MnCudto (monoclinic space group  $P2_1/c$ ).

In the real compound,  $[MnCu(dto)_2 \cdot 7.5H_2O]^0$  (Figure 3), the chains are waving along the  $x$  axis. The  $Mn^{2+}$  ions are "decorated" by three water molecules. The organization of the chains relies on the stacking of the  $CuS_4$  units along the  $z$  axis, building stacks of chains, separated by a bed of water molecules, part of an hydrogen bond network. This network of water molecules allows the stability of the crystal but is also a weak point of the structure. It was at the origin of the 1981 initial mistake: pumping for too long the dioxygen of the cryostat, at room temperature, withdrew the water-bed molecules, destroyed the separation between the stacks of chains, collapsed the crystal and masked the 1D ferrimagnetic behaviour. This was a lesson for future fragile materials: cool down to 100K before pumping the cryostat! It works well.

Other isostructural chains were produced with  $B = Mn$  when varying  $A$ :  $A = Cu, Ni, Pd, Pt$ .<sup>[1,13b]</sup>

The systematic use of complexes used as ligands to build solids with complex structures has become a successful synthetic strategy in molecular materials chemistry. Sections 8 and 9 give a few examples selected in our chemistry.

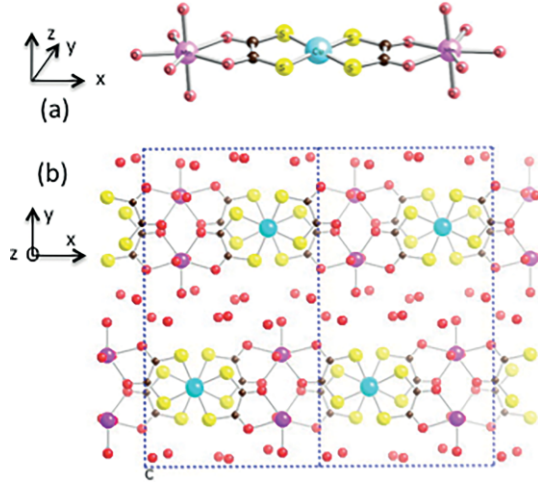


Figure 3. Structure of the first ferrimagnetic chain  $\text{MnCu}(\text{dto})_2 \cdot 7.5\text{H}_2\text{O}$ . (a) Perspective view of one chain. (b) View down  $z$  of waving neighbouring chains in the  $x,y$  plane, emphasizing the stacking at the Cu site and evidencing the water bed between the planes of chains. Colour code: light blue,  $\text{Cu}^{2+}$ ; violet,  $\text{Mn}^{2+}$ ; red, O; yellow, S.

## 6. Ferrimagnetic Chains: Expected Characteristic Magnetic Features

The deep knowledge accumulated in the study of homometallic 1D systems was useful to find how to represent and to compute the energy states of ferrimagnetic chains. Several groups of researchers (M. Drillon, D. Beltran, R. Georges) were engaged in such endeavours, parallel to ours.<sup>[11]</sup> In collaboration with the teams of J.-P. Renard at Orsay and of M. Julve in Valencia we used four approaches: (i) a qualitative one to demonstrate the presence of a minimum in the  $\chi_{\text{M}}T$  curve when the temperature is varying from ambient to 0K;<sup>[12]</sup> (ii) substituting the linear chain by a ring system of increasing radius and then approximating the thermodynamic properties of the infinite ring by extrapolating the results of finite rings of increasing sizes;<sup>[12,13]</sup> (iii) a “transfer matrix” approach;<sup>[13a]</sup> (iv) using a clever Hamiltonian imagined by J. Seiden, analytically solvable, where the system is approximated by an alternation of quantum spins 1/2 ( $\text{Cu}^{2+}$ ) and “classical” infinite spins (in place of  $S = 5/2$  for  $\text{Mn}^{2+}$ ).<sup>[13a,14]</sup>

This is the privilege of the inspired physicist to approximate a mere spin 5/2 by an infinite spin and so replace a quantum problem by a classical one.

(i) The qualitative demonstration, due to Kahn, considers that the ferrimagnetic system built by  $N$  pairs of spins  $S_A$  and  $S_B$  behaves at high temperature as a paramagnet with non interacting spins  $S_A$  and  $S_B$ , (since  $|J|/kT \ll 1$ ) and at low temperature as a paramagnet made of  $N$  correlated pairs of antiferromagnetically coupled spin  $S_A$  and  $S_B$ . The band energy of the system presents a ground spin state  $E_G$  with spin  $N(S_A - S_B)$  and a most excited state  $E_{\text{exc}}$  with spin  $N(S_A + S_B)$  – the highest spin value. At high T (HT), the system populates equally all the energy levels. The  $(\chi_{\text{M}}T)^{\text{HT}}$  value is finite. It is simply given simply by the Curie law:

$$(\chi_{\text{M}}T)^{\text{HT}} = \frac{N_A \beta^2 g^2}{3k} [S_A(S_A + 1) + S_B(S_B + 1)] \quad (4)$$

In this equation,  $N$  is the Avogadro constant,  $g$  the Lande factor,  $k$ , the Boltzmann constant and  $\beta = 1/kT$ .

At low T, the  $(\chi_{\text{M}}T)_{\text{LT}}$  value is:

$$(\chi_{\text{M}}T)^{\text{LT}} = \frac{N_A \beta^2 g^2}{3k} [N(S_A - S_B)^2 + |S_A - S_B|] \quad (5)$$

and therefore diverges with  $N$ .

The two limit values  $(\chi_{\text{M}}T)^{\text{LT}}$  and  $(\chi_{\text{M}}T)^{\text{HT}}$  are equal for  $N_0$ :

$$N_0 = \frac{S_A^2 + S_B^2 + 2S_{<}}{(S_A - S_B)^2} \quad (6)$$

Here,  $S_{<}$  is the lowest value of  $S_A$  and  $S_B$ . When  $N > N_0$ ,  $(\chi_{\text{M}}T)_{\text{LT}} \gg (\chi_{\text{M}}T)_{\text{HT}}$ .  $(\chi_{\text{M}}T)_{\text{LT}}$  diverges when  $N$  tends to infinite. It is easy to check that for  $S_A = 1$  and  $S_B = 1/2$ ,  $N_0 = 9$ . When increasing temperature from low temperatures, the first energy level to be depopulated is  $E_{\text{exc}}$ , the one of maximum spin  $N(S_A + S_B)$ . Therefore  $\chi_{\text{M}}T$  decreases. When decreasing  $T$  from high T, the first level to be depopulated is the one of highest spin and so  $\chi_{\text{M}}T$  decreases. In between the  $\chi_{\text{M}}T(T)$  curve *must* presents a minimum. This minimum is a characteristic feature of ferrimagnetic systems. In ref.<sup>[12]</sup> we reached the following general conclusion: “for a chain of alternated and antiferromagnetically coupled spins  $S_A$  and  $S_B$ ,  $\chi_{\text{M}}T$  first decreases when the compound cools down, then reaches a minimum for a finite temperature, and finally diverges when the temperature approaches zero”.

(ii) The approach by rings of increasing size  $(S_A, S_B)_N$  computes numerically, first the discrete energy levels of the different rings, then the corresponding magnetic susceptibility for a given ring at each temperature. Finally, an extrapolation to the values of an infinite ring (a ring of infinite radius becomes a linear chain, a trivial tool among 1D scientists) is done by assuming a variation of  $\chi_{\text{M}}T$  vs. the length of the chain  $N$ , such as:  $\chi_{\text{M}}T = (\chi_{\text{M}}T)_{\infty} + a/N^{\alpha}$ , where  $a$  and  $\alpha$  are coefficients depending on  $kT/|J|$ . The numerical results of the extrapolation, too bulky to be reproduced here, can be found in ref.<sup>[12]</sup> Tables II ( $J < 0$ ) and III ( $J > 0$ ). A graphical representation of the energy levels and of the magnetic properties are given in Figure 4. Are shown: the high T paramagnetic limit; the presence of the minimum and of uncorrelated MnCu spin pairs at the minimum, the susceptibility for the infinite chain diverging with the correlation of the MnCu spin pairs when T decreases.

The  $\chi_{\text{M}}T$  minimum is clearly observed.

(iii) The approach using successively Hamiltonians of different natures (quantum-classical or quantum-quantum) and a transfer matrix procedure, due to Renard and Seiden, is too long to be reported here and can be found in ref.<sup>[13a]</sup>.

(iv) Finally, the original quantum-classical Hamiltonian of Seiden allows to use the properties of the infinite classical spin (free continuous rotation) to solve the problem and to reach a very useful analytical expression of the susceptibility. M. V. used the Seiden formula in the appropriate range of temperature to fit the MnCu(dto) experimental data.

$$\chi_{\text{M}} = \frac{N_A \beta^2 \mu_B^2 JS}{6} (g_s S - \frac{J}{|J|} g_s s)^2 \quad (7)$$

M. V. drew Figure 5, published in the Seiden's paper,<sup>[14]</sup> which displays the comparison between the experimental sus-

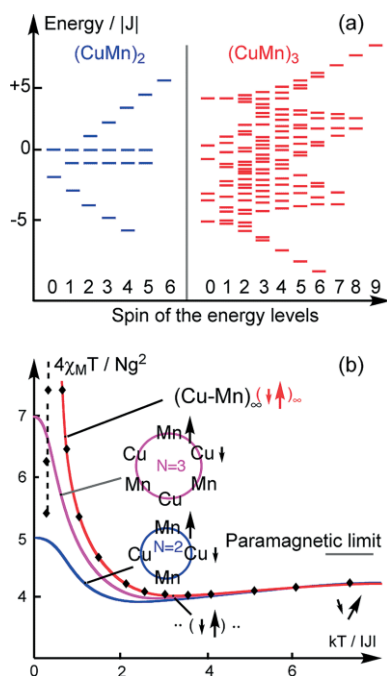


Figure 4. (a) Computed energy levels for two MnCu rings with  $N = 2$  (blue) and 3 (violet). (b) Thermal behaviour of the magnetic susceptibility (as  $\chi_M T$ ) in reduced quantities. Adapted with permission from ref.<sup>[13b]</sup> Copyright (1984) American Chemical Society. To the best of our knowledge, such a representation of spin levels appeared for the first time in the literature in ref.<sup>[13b]</sup>.

ceptibility of the MnCudto chain and the theoretical fit by the Seiden expression.

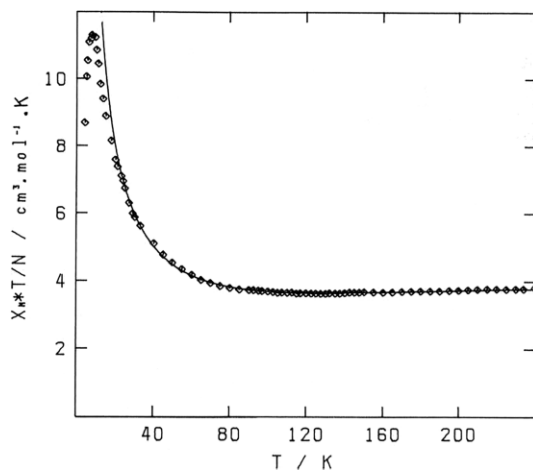


Figure 5. Fit of the experimental susceptibility data of MnCudto ( $\diamond$ ) by the Seiden's analytical expression.

The agreement is remarkable and gives the opportunity to extract a numerical value for the intramolecular coupling constant  $J_{MnCu} = -303 \text{ cm}^{-1}$ , a large value, which allows to observe easily the  $\chi_M T$  minimum at a rather high temperature. The divergence between the experiment and the fit at low temperature is obviously due to a departure from 1D behaviour, sign of an interchain antiferromagnetic interaction leading to a non-magnetic ground state.

The mathematical details of the four demonstrations can be found in refs.<sup>[12-14]</sup>

Similar steps were made in parallel by the group of Drillon at Strasbourg in collaboration with the team of Georges at Bordeaux. They examined different systems in relation with experimental data of MM'EDTA bimetallic chains based on the EDTA bridge (M, M' transition metal ions): ordered, paired, random Ising, z-z interactions alternation of J or g values and so on. A useful summary of the methods and conclusions of these authors can be found in a chapter of the book edited by O'Connor.<sup>[15a]</sup> Today, sad sign of our times, a review on molecular magnetism by one of the authors<sup>[15b]</sup> recalls his own work and simply forgets our contribution.

## 7. Ferrimagnetic Chains: an Exciting Dead-End towards 3D Magnets

An apparent nice "win". Nevertheless, life is difficult. To summarize, up to now, it was possible to synthesize the molecular MnCudto ferrimagnetic chain, to measure the magnetism of the solid, to observe experimentally the expected 1D behaviour thanks to the high antiferromagnetic intra-chain interaction  $J_{AF}$  and to launch a very fruitful collaboration with physicists. The  $\chi_M T$  minimum of the MM'(EDTA) systems studied at about the same time in Strasbourg, appears at much lower temperatures.<sup>[2]</sup>

We have seen in Figure 5 that the behaviour at low temperature departs from the theoretical curve and after a maximum, sharply decreases and tends to zero. The magnetic properties are measured not on one isolated 1D object but on the whole molecular solid. We need therefore to undertake a step further and to look at (i) the way the molecular chains are organized in the solid; (ii) their interchain interaction with a coupling constant  $j_{inter}$ . Figure 6 gathers a few possible situations. In a) two neighbouring ferrimagnetic chains present a ferromagnetic interchain interaction,  $j_f$ . If the interchain interactions are present in the three directions of space a ferrimagnetic solid arises. In b) two neighbouring ferrimagnetic chains display an antiferromagnetic interchain interaction,  $j_{af}$ . The magnetism of the ferrimagnetic chains are then cancelled and a 3D antiferromagnet

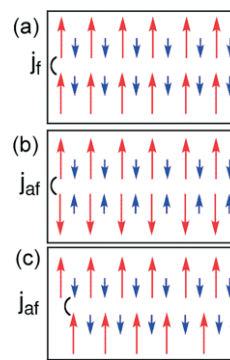


Figure 6. Three examples of interactions between ferrimagnetic chains in the solid: (a) ferromagnetic interaction,  $j_f$ ; (b) antiferromagnetic interaction,  $j_{af}$  between similar (big) spins; (c) antiferromagnetic interaction  $j_{af}$  between large and small spins.

results, with a complex spin structure. To observe the 1D ferrimagnetic behaviour, we need solids with the intra-chain antiferromagnetic interaction  $|J_{AF}| \gg |j_{af}|$ , the inter-chain interaction. If not, the expected minimum in the  $\chi_M T$  curve is not observed as we have seen in the accidentally modified MnCudto.<sup>[1,13b]</sup> To get a ferrimagnetic 3D ordered magnet, we need to control the inter-chain interactions and their topology. A clever solution was proposed by Kahn. It is sketched in Figure 6c: it consists “simply” in displacing one chain by half-a-cell parameter so that all the large spins are aligned parallel thanks to an antiferromagnetic interaction  $j_{af}$  between the large spins of one chain with the small spins of neighbouring chains.

A remarkable realization of his idea was implemented by Kahn and Pei<sup>[16]</sup> using the oxamate complexes Cupba and CupbaOH shown in Figure 7 (pba = 1,3-propylene-bis-oxamate; pbaOH = 2-hydroxy-1,3-propylene-bis-oxamate). The interest of such “molecular bricks” compared to Cudto or  $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$  is the enhanced stability of the complex and the possibility of substitution on the alkyl chain between the two nitrogen atoms. First, with the pba ligand, they obtained MnCupba chains antiferromagnetically coupled (Figure 8a). Then, they modified the hydrogen-bond network by introducing a hydroxyl group on the pba to get pbaOH and MnCuphaOH (Figure 8b).

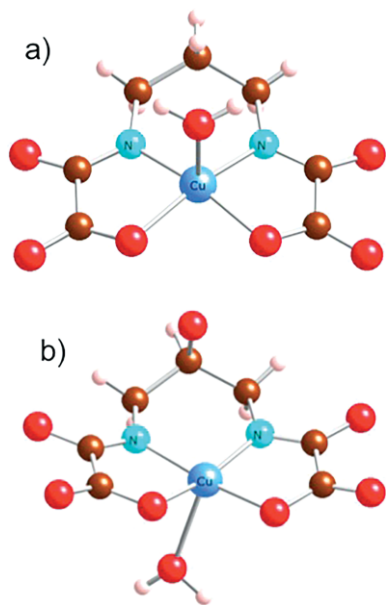


Figure 7. Molecular complexes used as ligands: (a) Cupba; (b) CupbaOH. Colour code: blue, Cu; light blue, N; red, O; brown, C; pink, H.

A second simple and brilliant chemical idea, which worked fairly well. The chain displacement was not exactly half a parameter but when M. V. measured the magnetism of this system along the three axes (on beautiful deep blue transparent single crystals grown by Pei) we were happy to observe the  $\chi_M T$  minimum and the divergence of  $\chi_M T$  at low T (Figure 9a) and a 3D ordering at 4.6K (Figure 9b).

The magnetization was performed on a wonderful very sensitive low magnetic field home-made SQUID in Renard’s laboratory. M. V. can confess that, cut after cuts, the final measurements were performed on a crystal weighting 4  $\mu\text{g}$ . This was

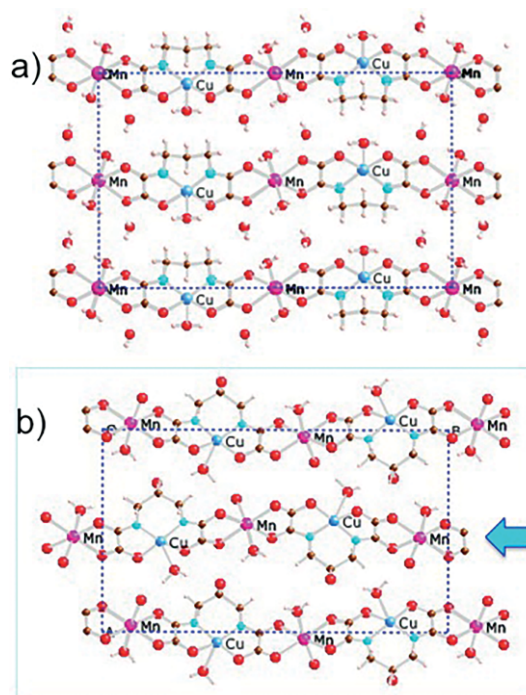


Figure 8. Projection of the crystal structures of (a) MnCupba and (b) MnCupbaOH. The bond network in (b) displaces one of the chains by almost one-half repeating unit and creates a weak interchain antiferromagnetic interaction between Mn and Cu instead of Mn and Mn in (a).

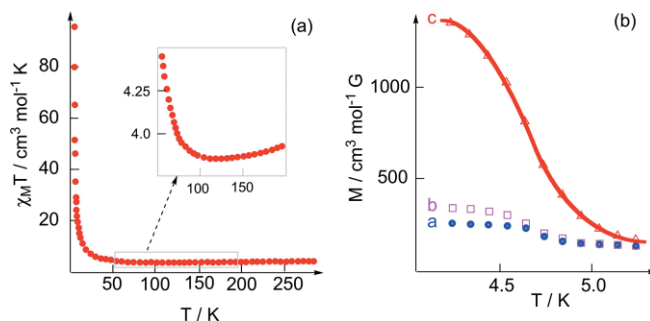


Figure 9. Magnetism of MnCupbaOH. (a) Thermal variation of  $\chi_M T$  of a microcrystalline sample. (b) Magnetization along the three crystallographic axes. The easy direction is along c. Adapted with permission from ref.<sup>[16]</sup> Copyright (1986) American Chemical Society.

the first solid made of 1D ferrimagnetic chains to present a 3D order at low temperature. Finally, we got a 3D magnet. Success.

Once more, the enthusiasm will be tuned by two last remarks. First, looking more closely to the structure thanks to Figure 9, one can realize that (i) the magnetization of the solid is anisotropic, the easy axis being along the c direction; (ii) the ferrimagnetic chains appear ordered. In the parallel *ab* planes, the interchain interactions are the ones requested. The *ab* planes are ferrimagnetic.

But what about the interaction between the *ab* planes? No obvious exchange interaction appears available, only *dipolar magnetic* interactions. M. V. computed the magnetic field created on an empty manganese site (green circle), thanks to a programme written by P. Beauvillain (Figure 10). The dipolar

field was directed along *c*. This aligns the magnetization of all the planes in the same direction, achieving a 3D ferrimagnet. If the dipolar field had been in the opposite direction, once more an antiferromagnetic order would have been observed.

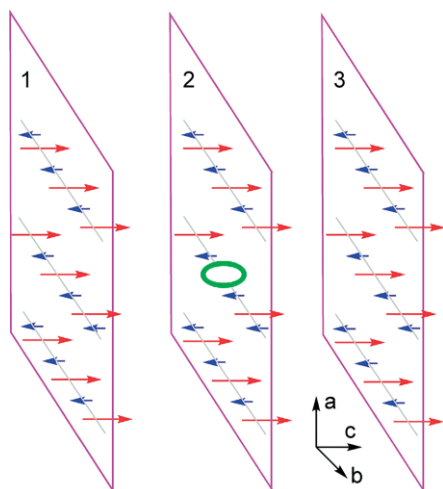


Figure 10. Schematic perspective view of the spin system of MnCupbaOH along the three axes *a*, *b*, *c* showing the approximate direction of spins. The green circle points an empty place where the dipolar magnetic field is computed.

The immediate (sad) conclusions are that (i) the magnetic dipolar effect, always present in magnetic solids, is here out of control, as often; (ii) we had, with the MnCu(pbaOH), brilliantly conceived, a lucky success; (iii) the 1D ferrimagnetic approach, even nice, is a dead end towards 3D magnetic order. A second remark, even more severe, can be drawn from thermodynamics: it is well known among the 1D scientists that long range order cannot exist in a 1D system, at  $T \neq 0K$ : if we imagine a perfectly ordered ferromagnetic chain with  $N$  sites and a  $J$  intra-chain exchange constant, the energetic cost to break the chain at some site  $i$  and to reverse one half the spins is  $J$ . It is possible to break the chain at  $N-1$  sites. The entropy gain so provided is  $kT \ln(N-1)$ . Hence:

$$\Delta G = \Delta H - T \cdot \Delta S = J - kT \cdot \ln(N-1) \quad (8)$$

$N$  tending towards infinite, the 1D ground state is disordered at  $T \neq 0 K$ . The demonstration, due to Landau can be extended to ferrimagnetic systems and to 2 D ones.

Around these years, at the turn of the 80s and 90s, significant steps happened in our respective professional lives and our ways diverged: A. G. joined the Laboratoire des Matériaux (presently Centre Interuniversitaire de Recherche et Ingénierie des MATériaux (CIRIMAT)) at Institut National Polytechnique de Toulouse to work in the CVD (Chemical Vapor Deposition) group (presently SURF), whereas M. V. left his chains at Orsay, where beautiful 1D systems continued to be actively studied by Kahn, Nakatani and others, and moved to Paris.

## 8. From 1D to 2D in Toulouse

A. G. activities were oriented towards MOCVD (Metal-Organic Chemical Vapor Deposition), which made it possible to keep a foot in the crystal chemistry of metal complexes with organic

ligands. But even then, one does not serenely leave the design of metal complexes with exciting physical properties to the design of metal complexes whose fate is to be thermally destroyed just to coat a surface with some functional material. Fortunately, it was the time of the tremendous fad for high temperature superconductors (HTSC). The CVD group had just joined a program on metalorganic precursors for the MOCVD growth of  $\text{LnBa}_2\text{Cu}_3\text{O}_7$  ceramics. Most ceramics of technological interest contain at least two metallic elements from the blocks *s*, *p*, *d* or *f* of the periodic table. Working on molecular precursors of  $\text{LnBa}_2\text{Cu}_3\text{O}_7$  gave the opportunity to focus on the organometallic chemistry of three cations respectively from blocks *s*, *d* and *f*. The interest increases when one of the objectives is to obtain single-source precursors, i.e. containing at least two of the elements to be deposited. Such heteropolymetallic complexes are likely to show other interesting physical properties (magnetism for instance) before undergoing thermal destruction.

Thus, in continuation of his earlier works, the research on heterometallic precursors led A. G. to work on mixed complexes of copper or nickel and *s* or *p* or *d* elements, using not only oxalate and dithiooxalate anions, but also squarate and dithio-squarate (see ref.<sup>[17]</sup> and refs. [2,3,6] therein) and then the beta-diketonate and alkoxide ligands conventionally used for the preparation of volatile metal complexes. This activity extended as part of an INTAS program coordinated by A. G.. Besides the Toulouse team, the program involved teams from Valencia (M. Julve), Padua (G. Battiston), Moscow (N. Kuzmina, A. Kaul) and Novosibirsk (I. Igumenov). This collaboration led to a series of possibly volatile heteropolymetallic complexes prepared according to the technique of assembling block complexes (for example  $M(\text{SB})\text{Ln}(\text{dik})_3$  with  $M = \text{Cu}, \text{Ni}$ ,  $\text{Ln} = \text{Y}, \text{La}, \text{Gd} \dots$ ,  $\text{SB} = \text{Schiff base}$ ,  $\text{dik} = \text{beta-diketonate}$ ). These brand-new complexes were submitted to single-crystal structure determination, magnetic measurements when appropriate, thermochemical studies, CVD experiments (see ref.<sup>[18]</sup> and refs.[9,15] therein).

Progressively, A. G. got more and more involved in specific MOCVD works such as the deposition of (i) thin Ni films from less dangerous precursors than  $\text{Ni}(\text{CO})_4$ ; (ii) copper lines for ULSI circuits; (iii)  $\text{TiO}_2$  to study the biocompatibility in function of the micro structure; (iii)  $\text{TiO}_2$  again, on micro-fibrous supports for photocatalytic application; (iv) lanthanide beta-diketonates to graft in mesoporous silicas for luminescent materials. The last years have been widely devoted to the preparation and structure-properties relationship studies of amorphous alumina thin films in view of catalytic application or protection against high-temperature oxidation.<sup>[19]</sup> This has been an opportunity for the crystal chemist to discover the exciting world of the amorphous state.

## 9. From 1D to 3D in Paris

In Paris, M. V. tried to imagine more reliable strategies to get 3D molecular magnets.

### 9.1. Conditions for Magnetic Ordering

An important step was the understanding of the conditions for a magnetic solid to present a long-range order, as proposed by



Renard (Table 1).<sup>[20]</sup> At the microscopic level, two main parameters control the transition, occurring at temperature  $T_C$ : (i) the dimensionality of the magnetic network (1D, chains; 2D, planes; 3D, frameworks); (ii) the anisotropy of the interaction according to the relative values of the effective components of the coupling constants  $J$ :  $J_x$ ,  $J_y$ ,  $J_z$ .

Table 1. Existence of long-range order at  $T \neq 0K$  in a magnetic system with short-range interactions, as a function of its dimensionality and anisotropy.

Dimensionality/ anisotropy	Name	1D	2D	3D
$J_z \gg J_x \approx J_y$	Ising	No	Yes	Yes
$J_x \approx J_y \gg J_z$	XY	No	KT <sup>[a]</sup>	Yes
$J_x = J_y = J_z$	Heisenberg	No	No	Yes

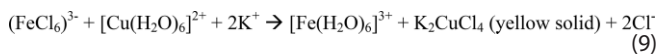
[a] A special transition bearing the name of Kosterlitz and Thouless (KT). (adapted from J.-P. Renard.<sup>[20]</sup>) 30 years later the Nobel Prize committee recognized the importance of such topological phases and transitions, associating F.D.M. Haldane (Haldane's gap) to the Award. The experimental characterization of the Haldane's gap and other gapped systems is another exciting long 1D saga.<sup>[21a]</sup> For a recent review, see <sup>[21b]</sup> for example. We cannot include in the volume allowed by this minireview the important situation of anisotropic molecules or chains, with zero-field splitting, presenting a long-range order without exchange interaction between the species. See ref.<sup>[21c]</sup>

The conclusion is then clear. 1D chains, first considered as a *conceptual* step from isolated molecules to magnetic ordered solid, are a *practical* dead-end. 2D planes can work within some constraints (Ising and KT transitions). The chemist willing to synthesize magnets should then create three-dimensional (3D) networks, which present long-range order, whatever the exchange anisotropy. We give a few examples below, relying on the synthetic strategy using complexes as ligands.

## 9.2. New Mononuclear Complexes to Build 3D Solids

Among M. V. attempts, three can be quoted: hexachloroferrate(III), hexacyanochromate(III) and the chiral tris-oxalato chromate (III).

M. V. and V. Gadet imagined in 1989, to use the hexachloroferrate(III) (octahedral,  $d^5$ ,  $(t_{2g})^3(e_g^*)^2$ , high spin), in combination with divalent transition metal ions of the first row. We began with copper(II). When aqueous solutions of potassium hexachloroferrate(III) and copper(II) chloride are mixed, a bright yellow solid precipitated. Exciting! The dream disappeared at the first analysis, which revealed a deceiving, but foreseeable, potassium tetrachlorocuprate(II).<sup>[22a]</sup>



This could have been expected from the rapid exchange of the chloride ligand in aqueous solution around the high spin  $d^5$   $\text{Fe}^{3+}$  ion, with two electrons in the antibonding  $e_g^*$   $d$  orbitals.

## 9.3. High $T_C$ Molecular Magnets

From this colourful remarkable failure, we drew two lessons: the starting complexes must be thermodynamically stable and kinetically inert. Cyanide should behave better than chloride

and  $(t_{2g})^6$  electronic configuration should be preferred to  $(e_g^*)^4$  ones, which is always true for hexacyanido complexes. We checked therefore the hexacyanidometallates  $[\text{B}(\text{CN})_6]^{n-}$ , essentially with  $n = 3$ , B(III) = Fe (low spin  $d^5$ ), Mn (low spin  $d^4$ ), Cr ( $d^3$ ). Cr(III) ( $d^3$ ,  $t_{2g}^3$ ,  $S = 3/2$ ) revealed to be the best choice (inert, with a half-filled electronic shell). We combined the hexacyanidometallates  $[\text{B}(\text{III})(\text{CN})_6]^{3-}$  with divalent transition metal complexes  $A^{2+}$  of the first row to get several families of Prussian blue analogues (PBA). The Kahn's exchange model was guiding the rational choice of both B and A transition metals to synthesize PBA with increasing Curie temperatures:  $\{\text{KNi}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  ( $T_C = 90$  K, ferromagnetic) by Gadet,<sup>[22b]</sup>  $\{\text{Cr}^{\text{II}}_3[\text{Cr}^{\text{III}}(\text{CN})_6]_2\}\cdot 15\text{H}_2\text{O}$  by Mallah ( $T_C = 240$ K, ferrimagnetic)<sup>[22c]</sup> and finally, a deep blue molecule-based room temperature magnet by Ferlay  $\{\text{V}^{\text{II}}_3[\text{Cr}^{\text{III}}(\text{CN})_6]_2\}\cdot 15\text{H}_2\text{O}$  with a  $T_C$  of 315 K (42 °C), the highest  $T_C$  for a rationally synthesized molecular magnet.<sup>[22d]</sup> The V/Cr stoichiometry is roughly 3:2 and the mean number  $z$  of magnetic neighbours is 4. A few years later, our competitor and friend, G. Girolami at Urbana reported a higher Curie temperature,  $T_C = 376$  K for the compound  $\{\text{KV}(\text{Cr}(\text{CN})_6)\}\cdot 3\text{H}_2\text{O}$ .<sup>[23]</sup> They used the same pairs of transition metal ions but a different stoichiometry V/Cr= 1 and  $z = 6$ . It is well known after Néel that the  $T_C$  is proportional to the number of magnetic neighbours. More results can be found in review papers<sup>[24]</sup> and book chapters.<sup>[25]</sup>

## 9.4. Multifunctional Magnets

The chiral tris-oxalato-chromate  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  when combined with transition metal ions  $A^{2+}$  provides chiral 2D or 3D frameworks with stoichiometry  $C^+A^{2+}[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ .  $C^+$  is a template, wrapped in the network. We then turned to the search for multifunctional materials. Following Hashimoto,<sup>[26a,b]</sup> A. Bleuzen, V. Marvaud and M. V. developed photomagnetism either with Prussian blue analogues<sup>[26c]</sup> or with octacyanomolybdate(V).<sup>[27]</sup> With  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ , M. Gruselle, C. Train and M. V. developed chemistry and physics of chiral magnets and demonstrated new exciting second order phenomena such as magnetochiral dichroism.<sup>[28]</sup> Such exciting stories are now in other creative hands.

## 10. Conclusion

We tried to show how, beyond the errors and mistakes, the seminal discovery of bimetallic ferrimagnetic chains based on the synthetic use of the concept "complex as ligand", combined with original creative ideas has irrigated the synthetic chemistry of brand new systems, room temperature magnets, photomagnetic and chiral magnets, functional surfaces. This work relies not only on the celebrated individual merits of the two so-called "Prize winners" (A. G. and M. V. 1984, still working together<sup>[29]</sup>), but on the active collaboration of many scientists, students or researchers, physicists and chemists during tens of years. Their names appear in the references: the presented achievements belong to them. Science is a collective adventure as witnessed by a recent special volume.<sup>[30]</sup> It is our duty and our pleasure, to thank all the actors of this human saga.

**Keywords:** Synthesis design · Chain structures · Heterometallic complexes · Magnetic properties · Ferrimagnetic chains

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