Magnetism: Molecules to Materials IV

Nanosized Magnetic Materials

Edited by
Joel S. Miller and Marc Drillon

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Preface

The development, characterization, and technological exploitation of new materials, particularly as components in 'smart' systems, are key challenges for chemistry and physics in the next millennium. New substances and composites including nanostructured materials are envisioned for innumerable areas including magnets for the communication and information sector of our economy. Magnets are already an important component of the economy with worldwide sales of approximately $30 billion, twice that of the sales of semiconductors. Hence, research groups worldwide are targeting the preparation and study of new magnets especially in combination with other technologically important properties, e. g., electrical and optical properties.

In the past few years our understanding of magnetic materials, thought to be mature, has enjoyed a renaissance as it is being expanded by contributions from many diverse areas of science and engineering. These include (*i*) the discovery of bulk ferro- and ferrimagnets based on organic/molecular components with critical temperature exceeding room temperature, (*ii*) the discovery that clusters in high, but not necessarily the highest, spin states due to a large magnetic anisotropy or zero field splitting have a significant relaxation barrier that traps magnetic flux enabling a single molecule/ion (cluster) to act as a magnet at low temperature; (*iii*) the discovery of materials exhibiting large, negative magnetization; (*iv*) spin-crossover materials that can show large hysteretic effects above room temperature; (*v*) photomagnetic and (*vi*) electrochemical modulation of the magnetic behavior; (*vii*) the Haldane conjecture and its experimental realization; (*viii*) quantum tunneling of magnetization in high spin organic molecules; (*viii*) giant and (*ix*) colossal magnetoresistance effects observed for 3-D network solids; (*x*) the realization of nanosize materials, such as self organized metal-based clusters, dots and wires; (*xi*) the development of metallic multilayers and the spin electronics for the applications. This important contribution to magnetism and more importantly to science in general will lead us into the next millennium.

Documentation of the status of research, ever since William Gilbert's de Magnete in 1600, provides the foundation for future discoveries to thrive. As one millennium ends and another beacons the time is appropriate to pool our growing knowledge and assess many aspects of magnetism. This series entitled Magnetism: Molecules to Materials provides a forum for comprehensive yet critical reviews on many aspects of magnetism that are on the forefront of science today.

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1 Bimetallic Magnets: Present and Perspectives

Corine Mathonière, Jean-Pascal Sutter, and Jatinder V. Yakhmi

1.1 Introduction

An important branch of the molecular magnetism deals with molecular systems with bulk physical properties such as long-range magnetic ordering. The first molecular compounds with spontaneous magnetization below a critical temperature were reported during the eighties [1, 2]. These pioneering reports encouraged many research groups in organic, inorganic, or organometallic chemistry to initiate activity on this subject, and many new molecule-based magnets have been designed and characterized. A tentative classification can arise from the chemical nature of the magnetic units involved in these materials – organic- or metal-based systems and mixed organic–inorganic compounds. Of materials based only on magnetic metal complexes, several families such as the oxamato, oxamido, oxalato-bridged compounds and cyanide-bridged systems play an important role in the field of molecular magnetism. This contribution focuses mainly on molecule-based magnets involving oxamato and oxamido complexes. The most extensively used spin carriers are 3d transition metal ions. The magnetic interactions between these ions are now well understood and enable the rational synthesis of materials. This aspect will be highlighted in the first part of this contribution. The heavier homologs from the second and third series have been envisaged only recently for the construction of heterobimetallic materials. In the second part of this chapter we will briefly discuss the very encouraging first results obtained with such ions.

In 1995 Olivier Kahn wrote a paper reviewing the magnetism of heterobimetallic compounds [3]. An important part of this review was devoted to finite polynuclear compounds, which can be considered as models for the study of exchange interactions. Magnetic ordering is a three dimensional property, however, and the design of a molecule-based magnet requires control of the molecular architecture in the three directions of space. The results obtained in bimetallic supra-molecular materials by our group and others show different features:

- the dimensionality can be controlled by the stoichiometry of the reagents during the synthesis or by the number of solvation molecules;

[1] This chapter is dedicated to the memory of Professor Olivier Kahn who passed away suddenly on December 8, 1999. Many of the illustrative examples used in this contribution are results obtained by his group.

- in a chemical system, the magnetic properties can be modulated by the nature of metallic ions;
- these systems can be studied by alternative techniques which are complementary of the magnetic studies.

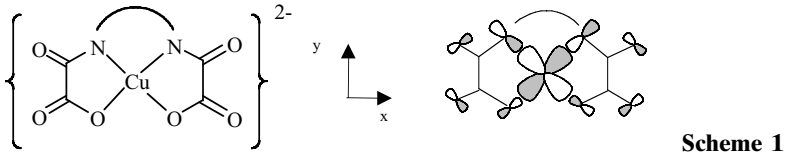
In the following text we will describe briefly the structures and magnetic properties of the compounds by emphasizing their main features. In particular, the magnetic properties will be summarized in terms of the exchange parameter J, the ordering temperature, T_C for a ferro(or ferri)magnetic material or T_N for an antiferromagnetic material, and the coercive field H_{coerc}, i. e. the magnetic field applied to cancel the permanent magnetization present in the material, which characterizes the hardness of a magnet.

1.2 Bimetallic Magnetic Materials Derived from Oxamato-based Complexes

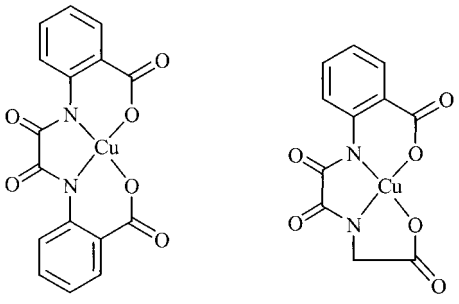
1.2.1 Dimensionality and Magnetic Properties

1.2.1.1 Cu^{II} Precursors

The general chemical strategy for the construction of bimetallic systems is based on the use of the bis-bidentate metal-complex as a complex-ligand. The bis-oxamato Cu precursors (shown in Scheme 1) and disymmetrical Cu^{II} complexes with two types of bridging units (oxamato and carboxylato) (shown in Scheme 2) have mainly been used for the preparation of extended bimetallic compounds.



Scheme 1



$[Cu(obbz)]^{2-}$ $[Cu(obze)]^{2-}$ **Scheme 2**

$[Cu(pba)]^{2-}$ (Table 1) was first described by Nonoyoma in 1976 [4] and at the end of the eighties it was used by Kahn and coworkers to design high-spin molecules, namely $(L\,M)_2Cu(pba)$ with $M = Mn^{II}$, Ni^{II}, L being a terminal ligand or bimetallic chains MCu(pba) [5, 6]. $[Cu(opba)]^{2-}$ was later synthesized by Stumpf; this precursor enables the preparation of compounds with different dimensionality – high-spin molecules [7], chain and ladders compounds, honeycomb layers, and interlocked compounds (Table 1) [8].

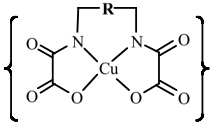
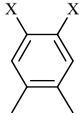
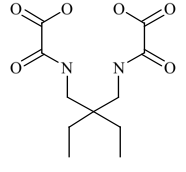
These Cu precursors were chemically modified through their ligand skeleton. The pba and opba ligands have been modified in two directions (Table 1):

- in the bridging moiety, by substituting the O (R_1 and R_2) atoms by N atoms, to increase the overlap of magnetic orbitals, because of the more pronounced diffuse character of the 2p(N) orbitals (next section);
- around the bridging moiety, by changing the nature of the R unit to modify the crystal packing of the molecules.

1.2.1.2 Mechanisms of Exchange Coupling

In the bimetallic systems obtained from reaction of Cu^{II} compounds with other transition metal ions, M, the magnetic ordering is ferrimagnetic. This means that exchange interactions between Cu and M ($S_{Cu} \neq S_M$ with S referring to the spin state of the metal) in the systems are a result of overlap between magnetic orbitals. If M has no orbital contribution (magnetically isotropic ion), the mechanism of the dominant Cu^{II}–M interactions through an oxamato (or oxamido)-bridge is well understood. In fact, both the planar structure of the Cu^{II} complex and the four peripheral oxygen atoms give to the compound its efficient mediating character in terms of magnetic connector. The Cu^{II} ion has one unpaired electron occupying a d_{xy} orbital which is delocalized toward the nearest nitrogen and oxygen atoms and also toward the external oxygen atoms (Scheme 1). This magnetic orbital may overlap strongly with magnetic orbitals of other ions linked to the Cu^{II} brick by the four external oxygen atoms. Structural investigations of several compounds in this family have shown that the distances between the two metals, Cu^{II}–M, is approximately 5.3 Å. Going further in the quantification of the exchange interactions, the magnetic data can be interpreted in the paramagnetic regime with a phenomenological Hamiltonian in a spin-spin coupling scheme such as $H = -J\mathbf{S}_{Cu} \cdot \mathbf{S}_M$, where J is the isotropic interaction parameter. For example, in Cu^{II}–Mn^{II} pairs, J has been found to be approximately $-30\,cm^{-1}$. On the basis of experimental studies (magnetism and neutron diffraction) and theoretical investigations (DFT calculations), the dominant mechanism is spin delocalization from the Cu^{II} ion towards the planar skeleton of the N(O)–C–O bridging part of the ligand. A similar situation occurs for the Cu^{II}–Ni^{II} pair, with additional Ni^{II} local anisotropy treated with the phenomenological zero-field splitting. The resulting J is higher, and has been estimated at $J = -100\,cm^{-1}$. For other couples, for instance Cu^{II}–Co^{II}, Cu^{II}–Fe^{II}, and Cu^{II}–Ln^{III}, the orbital contribution renders the interpretation of magnetic data using the simple scheme described above extremely difficult. For these species only qualitative interpretation of magnetic data has been achieved in order to determine the nature of exchange interactions between Cu^{II} and the other ion.

Table 1. Bis-oxamato Cu^{II} building blocks and resulting bimetallic compounds (M stands for magnet and m for metamagnet).

$[Cu^{II}L]^{2-}$ = 				Bimetallic compound			
Ligand skeleton (R)	R_1 and R_2	Ligand abbreviation	Cluster	Chain	Ladder	Plane	Interlocked planes
	Y = OH	O	pbaOH		√ (M)			
	Y = H	O	pba	√	√ (m)			
	X = H	O	opba	√	√ (m)	√ (M)	√ (M)	√ (M)
		O and NMe	Meopba				√ (M)	
		NMe	Me_2opba				√ (M)	
		N–$(CH_2)_n$–C_6H_5	$PhMe_2$opbox				√ (M)	
		n = 1, 3, 4	$PhPr_2$opbox				√ (M)	
			$PhBu_2$opbox				√ (M)	
	X = Cl	O	opbaCl_2	√				
		O	bis-pba	√				

1.2.1.3 Discrete Molecules

One of the first high-spin molecules was prepared in 1988. By using $[Cu(pba)]^{2-}$ as the core and $[Mn(Me_6\text{-}[14]ane\text{-}N_4)]^{2+}$ as a peripheral complex it is possible to obtain a trinuclear linear $CuMn_2$ species [5]. No single crystal was obtained, and a structure in agreement with the magnetic properties was proposed. The compound has ferrimagnetic behavior with an irregular spin state structure resulting from the antiferromagnetic interaction between the peripheral Mn ions ($S_{Mn} = 5/2$) and the middle Cu ion ($S_{Cu} = 1/2$). The low-temperature magnetic behavior is characteristic of a high-spin ground state equal to $S = 9/2$. Efforts were later made to obtain structural information for such species [9]. Let us mention the result of Liao's group. They succeeded in isolating crystals of binuclear and trinuclear compounds with the Ni^{II} ion ($S_{Ni} = 1$) [7]. The compounds are obtained by reaction of CuL^{2-} (L = pba, pbaOH and opba) with NiL^{2+}, L being tetraamine ligands, the final compounds having formula (L Ni)CuL or $(L\,Ni)_2CuL^{2+}$ (the trinuclear species is shown in Fig. 1). The compounds have been magnetically characterized, and have the expected ferrimagnetic behavior with an $S = 3/2$ ground state with a zero-field splitting.

An other interesting example has been described by Ouahab and Kahn with the $opbaCl_2$ ligand (Table 1) and its Cu^{II} complex [10]. The reaction of the Cu^{II} precursor with ethylenediamine, en, and Mn^{II} in the solvent DMSO led to an unprecedented trinuclear species $Mn^{III}Cu^{II}Mn^{III}$. The structure of this species has been resolved (Fig. 2), and reveals that:

- the Mn^{III} has replaced the Cu^{II} in the cavity N_2O_2 of the $opbaCl_2$ ligand;
- the formation of the $[Cu(en)_2]^{2+}$ complex, because of the strong affinity of the en for the Cu^{II}; and, finally,
- the self-assembling process between the anionic $[Mn(opbaCl_2)]^{-}$ and the cationic $[Cu(en)_2]^{2+}$ complexes.

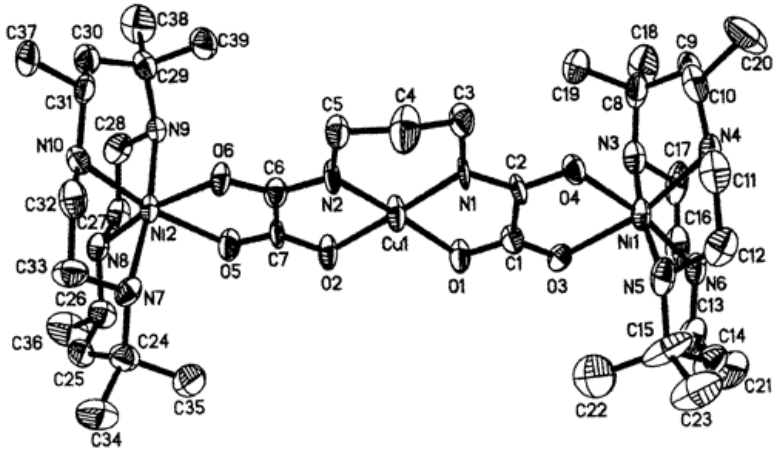


Fig. 1. Structure of the trinuclear cation $[\{Ni(cth)_2\}Cu(pba)]^{2+}$ [7] (reproduced with permission; Copyright 2001, the American Chemistry Society).

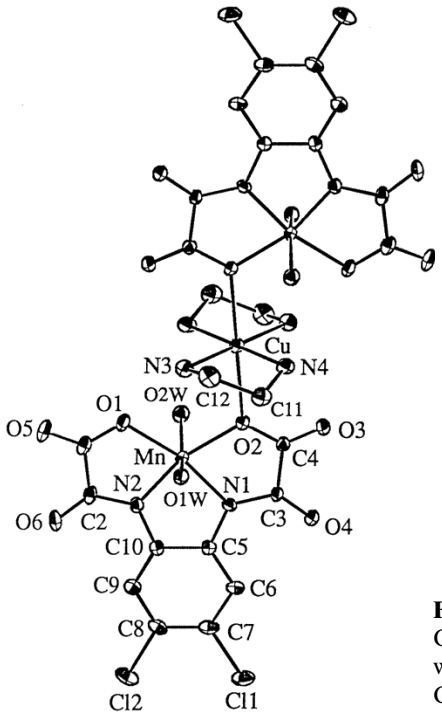
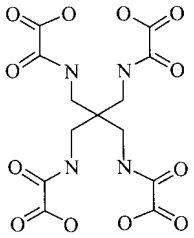


Fig. 2. Structure of the trinuclear species $Cu(en)_2Mn(Cl_2opba)(H_2O)_2$ [10] (reproduced with permission; Copyright 2001, the American Chemistry Society).

The linkage between the two complexes is realized through apical Cu–O bonds of length 2.454 Å. The delocalization of the spin density of the Cu^{II} towards the oxygen atoms in the apical position has been postulated to be negligibly small, and the magnetic data have been interpreted in terms of zero-field splitting of the Mn^{III} ion.

More recently, Journaux et al. obtained an interesting dinuclear $Na_4[Cu_2(bis\text{-}pba)]$ species by use of the bis-tetradentate ligand denoted bis-pba (Table 1 and Scheme 3) [11]. They succeeded in isolating dinuclear $Na_4[Cu_2(bis\text{-}pba)]$ species, with weak intramolecular ferromagnetic interactions between the two Cu^{II} ($J \approx 1\,cm^{-1}$). The reaction of this dinuclear compound with four equivalent external complexes such as $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) in acetonitrile or with $[Cu(tmen)]^{2+}$ (tmen = *N*, *N*, *N*, *N*-tetramethylethylenediamine) in water affords hexanuclear anionic compounds of formula $\{Ni(cyclam)\}_4Cu_2(bis\text{-}pba)$ and $\{Cu(tmen)(H_2O)\}_2\{Cu(tmen)\}_2\{Cu_2(bis\text{-}pba)\}$, respectively [12]. The structure of the Cu_6 species is shown in Fig. 3. It is made of two symmetry-related oxamato-bridged trinuclear units connected through the central carbon. In these hexanuclear species, the interactions through the oxamato bridge were found to be equal to $J = -342\,cm^{-1}$ for Cu_6 and $-82\,cm^{-1}$ for Cu_2Ni_4. The weak ferromagnetic coupling between the two Cu^{II} ions within the dinuclear synthon was masked by intermolecular interactions and/or local anisotropy.



$[Bis\text{-}pba]^{8-}$ **Scheme 3**

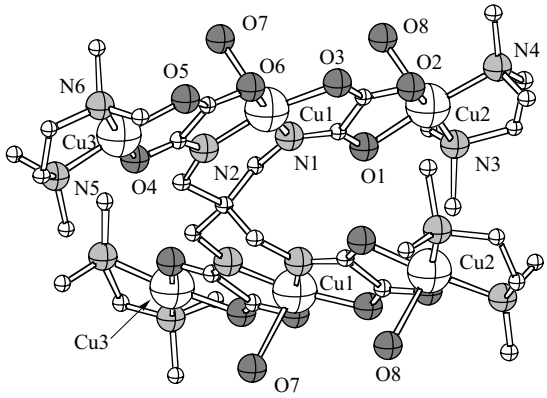


Fig. 3. Structure of the cationic hexanuclear unit $[\{Cu(tmen)(H_2O)\}_2\{Cu(tmen)\}_2\{Cu_2(bis\text{-}pba)\}]^{4+}$ [12] (reproduced with permission from Journal of Inorganic Chemistry).

1.2.1.4 One-dimensional Systems: Chain Compounds

When the dianionic Cu precursor is reacted with a 3d metal cation, M^{n+}, under stoichiometric conditions 1:1, neutral compounds of formula $MCuL_xS$ are obtained, S standing for solvent molecules. Different bimetallic chains have been structurally and magnetically described. The bimetallic chains with $M = Mn^{II}$ are described in detail in the review written in 1995 by Kahn. A typical example of a linear bimetallic chain is presented in Fig. 4. The magnetic properties of the chain compounds are well understood in the paramagnetic region (5–300 K), and are analyzed with theoretical models for ferrimagnetic one-dimensional systems, because of antiferromagnetic coupling between two different spins ($S_{Mn} = 5/2$ and $S_{Cu} = 1/2$) [13]. Below 5 K magnetic ordering occurs because of interchain interactions, which are governed by the crystal packing of the chains in the lattice. Actually, only one compound has ferromagnetic (F) ordering, with $T_C = 4.6$ K, namely $MnCu(pbaOH)(H_2O)_3$, which was the first molecule-based magnet belonging to the family described here [2]. Other compounds have antiferromagnetic (AF) ordering with T_N between 1.8 K and 5 K. The occurrence of F or AF magnetic ordering in these chain compounds is related to the interchain metal-metal separations of the type Mn–Cu for ferromag-

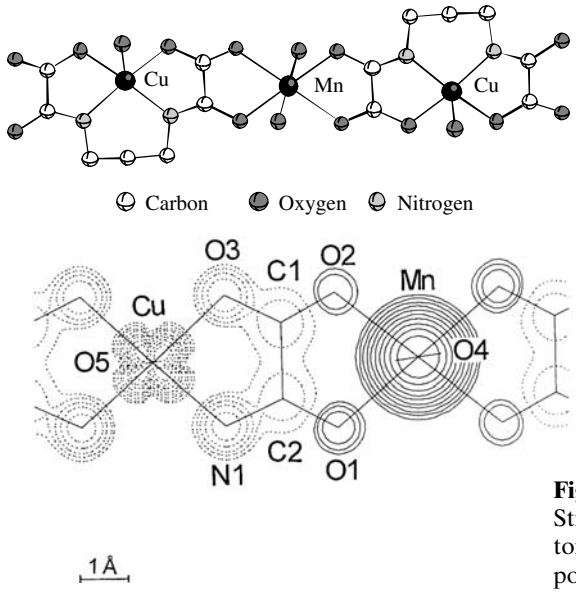


Fig. 4. $MnCu(pba)(H_2O)_3 \cdot 2H_2O$ (top) Structure of the chain compound (bottom) Spin density map deduced from polarized neutron diffraction data.

nets and Mn–Mn and Cu–Cu for antiferromagnets [14]. Some of these antiferromagnets behave as metamagnets, where a small applied magnetic field (between 1 or 2 kOe) can overcome the weak antiferromagnetic interchain interactions to induce a long-range ferromagnetic-like ordering. Note that for a few compounds there is no evidence of cooperative magnetic phenomena down to 1.8 K. They behave as quasi-perfect one-dimensional ferrimagnets; one example is $MnCu(opba)(DMSO)_3$ which has a zigzag chain structure [15].

Two interesting features of these bimetallic chain compounds can be mentioned in this section. First, the size of crystals (up to 15 mm^3) of $[MnCu(pba)(H_2O)_3] \cdot 2H_2O$ (Fig. 4) enabled the performance of further physical studies such as polarized neutron diffraction (p. n. d.) and optical spectroscopy (Section 1.2.4) [16, 17]. Secondly, the magnetic properties of compounds of formula $[MnCu(pbaOH)] \cdot xH_2O$ are strongly dependent on the water composition. Just above we mentioned the compound $MnCu(pbaOH)(H_2O)_3$, which behaves as a magnet at 4.6 K. It is possible to isolate another phase of this compound, $MnCu(pbaOH)(H_2O)_3 \cdot 2H_2O$, which has three-dimensional antiferromagnetic ordering in zero fields with $T_N = 2.4$ K. The bimetallic chains in both compounds are identical but in the latter the hydrogen-bond network developed by the non-coordinated water molecules imposes crystal packing with short interchain Mn–Mn and Cu–Cu separations, inducing antiferromagnetic interactions between the chains. The compound also has metamagnetic behavior, because a field of 0.9 kOe is sufficient to overcome these interchain interactions giving rise to a ferromagnetic state [14]. When $MnCu(pbaOH)(H_2O)_3$ is heated to 130°C one water molecule bound in the apical position of the copper coordination sphere is removed, and the new compound, $MnCu(pbaOH)(H_2O)_2$, has long range ferromagnetic ordering at $T_C = 30$ K [18]. The release of H_2O reduces

the interchain distances, and this enhances the interchain exchange interactions by a factor of 40. In Section 1.2.3 we will encounter other examples of magnetic ordering controlled by the water content of the material; these lead to the concept of magnetic sponges.

1.2.1.5 Two-dimensional Systems: Layered Honeycomb Compounds

We have seen that magnetic ordering of chain compounds can occur, and is strongly related to solvent molecules which impose the organization of the crystal packing. The interchain magnetic interactions remain weak, however, and magnetic ordering occurs at low temperature. To increase these temperatures, chemists have to build compounds with higher dimensionality. This section is devoted to bidimensional compounds, which are prepared with the same building blocks as the one-dimensional compounds but with different stoichiometries. Almost all of these 2D compounds behave as ferrimagnets. Experimentally the long-range magnetic ordering is revealed by the temperature dependencies of the field-cooled magnetization (FCM, which is measured by cooling the sample within a very small field, usually $H < 20\,\mathrm{Oe}$) and by the in-phase (χ'_M) and out-of-phase (χ''_M) molar susceptibilities in the ac mode. The non-zero value of χ''_M indicates the presence of permanent magnetic moment within the sample. The critical temperatures, denoted T_C, are determined by the extremum of the derivative curve d(FCM)/dT or by the maximum of the χ'_M curve, if it exists. In both instances they correspond to the temperatures where remnant magnetization vanishes, the latter is measured by turning the field off at low temperature and then warming up the sample in strictly zero field. The field dependence of the magnetization measured at low temperature enables the determination of the coercive field.

The reaction of $(NBu_4)_2$[Cu(opba)] with Mn^{II} in DMSO in 3:2 stoichiometry yielded a compound of formula $(NBu_4)_2[Mn_2\{Cu(opba)\}_3,4DMSO]\cdot 2H_2O$, which is a ferrimagnet below $T_\mathrm{C} = 15\,\mathrm{K}$ [15]. When Mn^{II} is replaced by Co^{II}, T_C increases to 29 K [19]. Unfortunately, no crystals were obtained for these compounds; a layered honeycomb structure was proposed for the anionic part (Fig. 5), for compatibility with the chemical formulas of the compounds and, of course, with the magnetic ordering occurring for temperatures higher than for the chain compounds. A theoretical approach was developed for a two-dimensional hexagonal model to derive an analytical expression for the molar magnetic susceptibility, χ_M, in the paramagnetic regime (40–300 K) using high-temperature expansions of the partition function [20]. Comparison of theory and experiment led to determination of the exchange parameter as $J = -33.1\,\mathrm{cm}^{-1}$, which is close to values obtained for related finite or chain compounds.

The occurrence of magnetic ordering in these two dimensional compounds might result from intralayer magnetic anisotropy and/or interlayer interactions. The cations are probably located between the anionic layers, and it is possible that the magnetic properties of these materials can be tuned by changing the size of the cations and/or slight modification of the ligand. Table 2 summarizes the different results. The magnetic behavior of the Mn derivatives strongly depends on the size

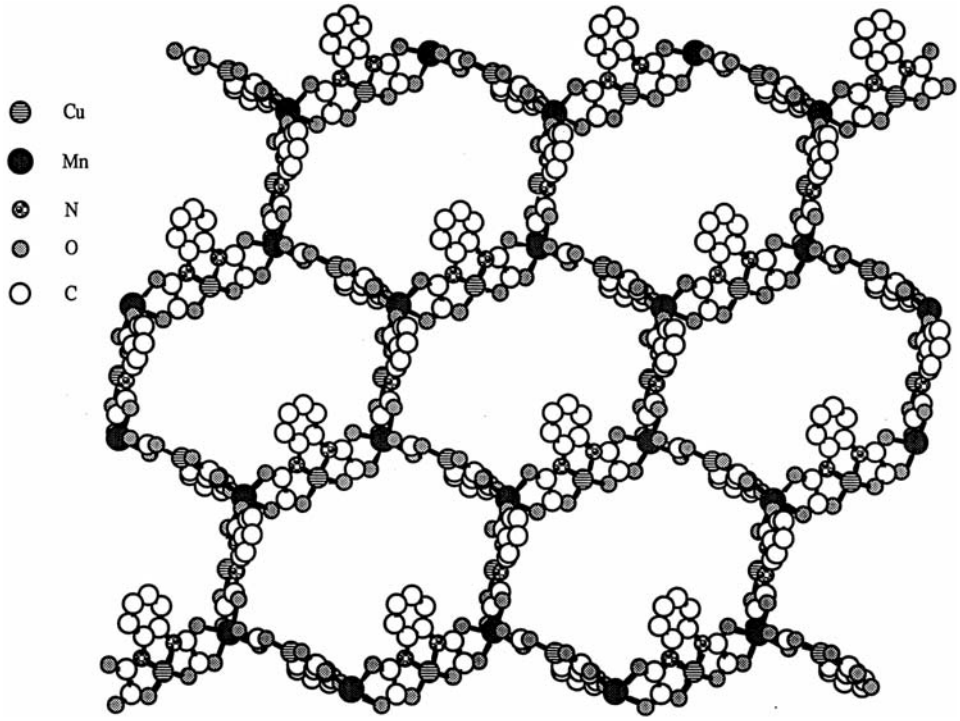


Fig. 5. Structure of a honeycomb layer.

of the cations. For large cations such as $[Ru(bipy)_3]^{2+}$ magnetic ordering occurs at lower temperature [21], and for small cations such as alkali metals, the compounds have weak ferromagnetism [19], because of competition between antiferromagnetic interlayer interactions and ferrimagnetic intralayer interactions. In contrast, all the Co compounds are ferrimagnets with $T_C \approx 30\,K$, irrespective of the cation. Such similar magnetic properties strongly suggests that the compounds adopt the same structure.

For some of these compounds XANES and EXAFS studies showed that each Mn^{II} is surrounded by three CuL complexes [22]. Journaux et al. compared experimental magnetic data with two theoretical models. One is based on a two-sublattice molecular field model in the mean field approximation, and is assumed valid for three-dimensional structures. The second already introduced above is adapted for hexagonal honeycomb layers. For all the examples studied the second approach led to good fitting of the magnetic data, and gave J values in good agreement with those deduced previously for other compounds of lower dimensionality. These structural and magnetic results lead to the conclusion that all these compounds are two-dimensional, with a honeycomb layered structure.

Finally, introduction of a cation with an intrinsic property, for instance chirality for cations such as nicot and ambutol or the paramagnetic $[FeCp_2^*]^+$, has been envisaged [23, 24]. Chirality was introduced with the objective of inducing the for-

Table 2. Magnetic properties for the family of oxamato(oxamido)-bridged honeycomb layered ferrimagnets of formula $Cat^{I}_{2}[M^{II}_{2}(CuL)_3]$ and $Cat^{II}[M^{II}_{2}(CuL)_3]$.

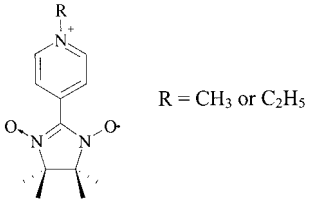
M^{II}	L	Cat	J (cm^{-1})	T_C (K)	H_{coerc} (Oe)	Ref.
Mn	opba	NBu_4^+	−32	15	<10	[15]
		NEt_4^+		17	<10	[19]
		NMe_4^+		$T_N = 15$ K		[19]
		K^+		$T_N = 15$ K		[19]
		Na^+		$T_N = 15$ K		[19]
		$FeCp^{*+}_2$		14	<20	[24]
		$CoCp^{*+}_2$		13	<20	[24]
		nicot^{2+}		$T_N = 15$ K		[23]
		ambutol$^+$		$T_N = 15$ K		[23]
		$Ru(bipy)^{2+}_3$		12		[21]
		PPh_4^+	−31.8	11.5	10	[22]
	Meopba	PPh_4^+	−32.6	13	10	[22]
	Me_2opba	PPh_4^+	−30.5	8	10	[22]
	$PhMe_2$opbox	PPh_4^+		12.5	5	[26]
	$PhPr_2$opbox	PPh_4^+		11.5	5	[26]
	$PhBu_2$opbox	PPh_4^+		13.5	5	[26]
Co	opba	NBu_4^+		30.5	1400 (5 K)	[15]
		NMe_4^+		33		[19]
		Cs^+		34		[19]
		K^+		33.5	2000 (5 K)	[19]
		Na^+		31.5		[19]
		$FeCp^{*+}_2$		27	3500	[24]
		$CoCp^{*+}_2$		27.5	5300	[24]

Notes: $Cp^* = C_5Me_5$, nicot is the chiral *N,N*-dimethylnicotinium species and ambutol is the chiral dimethylhydroxymethyl-2-ethylhydroxymethyl-1-propylammonium species.

mation of three dimensional coordination polymers in the same manner as for the 3D lattices obtained for the oxalato-bridged family discussed in another chapter of this series [25]. The magnetic cation was expected to increase the magnetic interaction between the layers, but the results were slightly disappointing, because no significant modifications of the magnetic properties were observed. These observations are, however, informative because they suggest future directions which might afford three-dimensional molecule-based magnets. In fact, a chiral cation can induce the formation of magnetic helicates only if it correctly fills the cavities formed by the three dimensional lattice. This obviously did not happen with the examples given above. Another way of filling the cavities of the anionic network is to use bulky ligands. The results obtained with the bulkier PhR_2opbox ligands (Table 1) designed on the basis of this strategy are not conclusive [26]. Note that the compound obtained with $[FeCp^*_2]^+$ enabled a Mössbauer study which revealed that the Fe^{III} ion begins to feel an internal field only at temperatures well below T_C. This clearly indicates that the cation between the layers is not directly involved in the long range magnetic ordering.

1.2.1.6 Interpenetrated Two-dimensional Networks: Interlocked Compounds

To increase the dimensionality further Kahn and coworkers imagined the use of a cation which would be capable of bridging two transition metal ions and which would be paramagnetic, thus increasing the magnetic density of the compounds. Cations belonging to the nitronyl nitroxide family, in which the unpaired electron is equally shared between the two N-O groups, have been envisaged (Scheme 4).



Scheme 4

The methyl and ethylpyridinium radical cations were used with success [27-29]. The structures of compounds with the formula $(Etrad)_2[M_2\{Cu(opba)\}_3]$ have been investigated by single crystal X-ray studies for M = Mn, Co, and by powder X-ray studies for M = Mg, Ni [30, 31]. All the compounds are fully interlocked with a general architecture made of two equivalent two-dimensional networks, denoted A and B, each consisting of parallel honeycomb layers. Each layer is made up of edge-sharing hexagons with an M^{II} ion at each corner and a Cu^{II} ion at the middle of each edge (Fig. 5). The layers stack above each other in a graphite-like fashion, with a mean interlayer separation of 14.8 Å. The A and B networks are almost perpendicular to each other, and interpenetrate in such a way that at the center of each hexagon belonging to a network is located a Cu^{II} ion belonging to the other network (Fig. 6). The networks are further connected through the radical cations; this affords infinite chains of the kind Cu_A–Etrad–Cu_B–Etrad, where Cu_A and Cu_B belong to the A and B network, respectively.

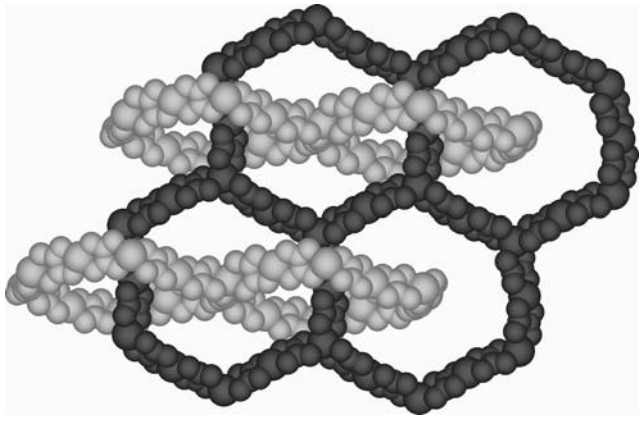


Fig. 6. Interpenetration of the two networks A and B.

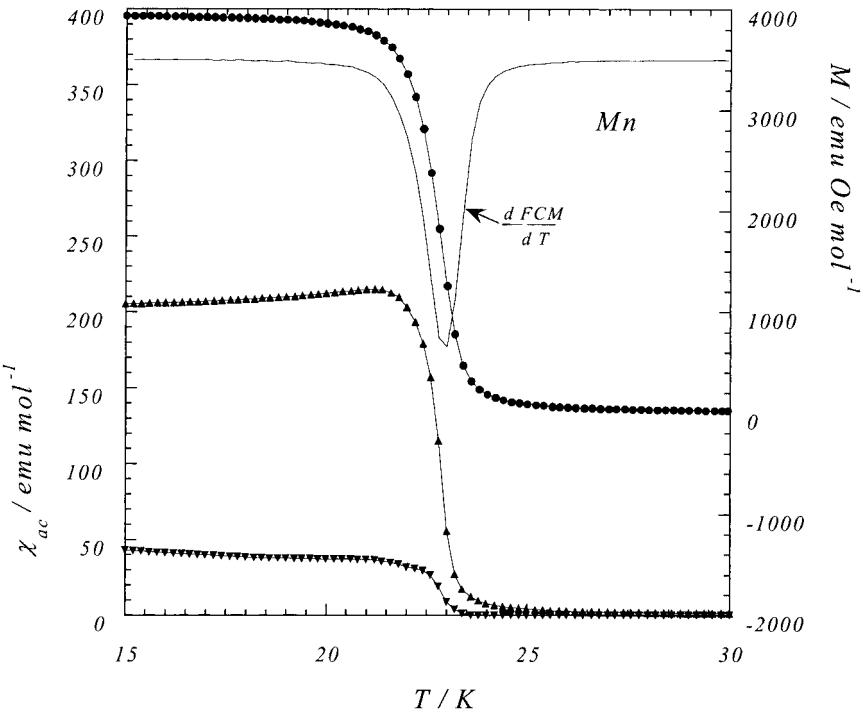


Fig. 7. FCM curve (•) and its derivative d(FCM)/dT (top) and in-phase χ'_M (▲) and out-of-phase χ''_M (▼) plots of ac susceptibilities (bottom) against T for (Etrad)$_2$[Mn$_2${Cu(opba)}$_3$].

Besides the aesthetic aspect of the structures, the compounds also had interesting magnetic properties. They behave as ferrimagnets with Curie temperatures in the range of 22–37 K (Figs. 7 and 8 and Table 3). The χ'_M and χ''_M curves can have two different general shapes, (i) a shape similar that of the FCM with $\chi'_M \gg \chi''_M$ as shown in Fig. 7, or (ii) a peak-like shape as shown in Fig. 8 with maximum values for very close temperatures. These differences are related to the coercivity of the material, case (i) applies for a very weak coercivity ($H_{coerc} < 10$ Oe) and case (ii) when a

Table 3. Magnetic properties for the family of oxamato(oxamido)-bridged interlocked ferrimagnets of formula (r-Rad)$_2$[M$_2^{II}$(CuL)$_3$], where r = methyl- or ethylpyridinium.

M^{II}	L	Cat	T_C (K)	H_{coerc} (Oe)	Ref.
Mn	opba	Merad	23	<10	[15]
		Etrad	22.8	<10	[29]
Co	opba	Merad	34	3000 (5 K)	[15]
		Etrad	37	8500–24 000	[29]
Ni	opba	Etrad	28	500	[30, 31]
Mg	opba	Etrad	Paramagnet	Paramagnet	[31]

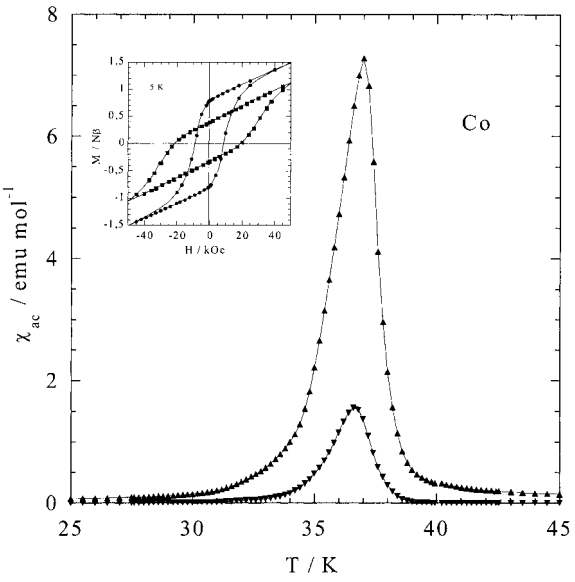


Fig. 8. In-phase χ'_M (▲) and out-of-phase χ''_M (▼) ac susceptibilities (bottom) for $(Etrad)_2[Co_2\{Cu(opba)\}_3]$. The insert shows the field dependence of the magnetization for two samples with the largest (•) crystals and smallest (■) crystals.

significant coercivity ($H_{coerc} > 1000$ Oe) exists. As a result of the formation of the 3D networks the Curie temperatures are effectively increased by up to 8 K for the Mn and Co compounds, compared with the layered compounds (Table 2). But the increase of T_C seems weak with regard to the three-dimensional connectivity of the compound. In fact, the interaction between the interlocked layers is weak, and has been estimated in $(Etrad)_2[Mg_2\{Cu(opba)\}_3]$. Because the Mg ion is diamagnetic, magnetic interactions occur only along the Cu_A–Etrad–Cu_B–Etrad chains. They are ferromagnetic, as expected between Cu^{II} and a nitroxide group occupying the apical position. Neglecting intermolecular interactions, the magnetic data were analyzed by a chain model for $S = 1/2$ spins, leading to an exchange parameter of $J = 8\,cm^{-1}$, which is four times weaker in absolute values than the intralayer interaction [31].

1.2.1.7 Ladder and Honeycomb Lattices in 3d–4f Systems

The chemistry of the bis-bidentate Cu-oxamato complexes is not limited to the reaction with 3d transition metals. Impressive extended structures have been obtained when $[Cu(opba)]^{2-}$ was reacted with lanthanide ions, Ln^{III}. The first compounds of this kind were reported in 1992 for the Ln^{III}–Cu(pba) system [32]. Two different structures have been described for compounds of general formula $Ln_2\{Cu(pba)\}_3$. One consists of discrete ladders of Ln going from Tb to Yb, and Y, an architecture similar to that of $Ln_2\{Cu(opba)\}_3$ shown in Fig. 9. The second results from condensed ladder-like motifs with a rearrangement of the rungs and is formed with Ln