Molecular Magnetic Sponges

Olivier Kahn,*[a] Joulia Larionova,[a] and J. V. Yakhmi[b]

Abstract: Some molecular magnetic materials behave as sponges. They can reversibly release or reabsorb water, both noncoordinated and coordinated, a process which is accompanied by a dramatic change of structure and of magnetic properties. When the sponges are hydrated, or wet, the structure consists of isolated units with a nonmagnetic ground state. When the sponges are dehydrated, or dry, the units are linked to each other, affording polymeric molecule-based magnets. Some of them exhibit a strong coercivity. $[CoCu(obbz)]\cdot n\,H_2O$ (obbz = *N,N'*-bis(2-carboxyphenyl)oxamido) represents a perfect example of such a situation. The starting material, $[CoCu(obbz)(H_2O)_4]\cdot 2\,H_2O$ with a nonmagnetic ground state, has a zero-dimensional structure. The trihydrate behaves as a one-dimensional ferrimagnet, and the monohydrate as a two- or three-dimensional ferrimagnet with a long-range magnetic ordering and a wide magnetic hysteresis loop. Upon rehydration, the tri- and monohydrates return to the initial hexahydrate form with a nonmagnetic ground state.

Keywords: ferrimagnets · ferromagnets · hysteresis · magnetic properties · polymerizations

Introduction

The field of molecule-based magnets is a new branch of chemistry, which deals with the design of molecular compounds exhibiting a spontaneous magnetization below a critical, T_c, and the study of their physical properties.[1] The very first compounds of this kind were reported in 1986,[2–5] and in the last few years an increasing number of research groups have initiated some activity along this line.

The typical synthetic approach to design molecule-based magnets consists of starting from precursors bearing a spin, then to assemble them in such a way that there is no compensation of the spins at the scale of the crystal lattice. When two spin carriers, A and B with the spins S_A and S_B, respectively, are close enough to each other, they interact; S_A and S_B are not good quantum numbers anymore. The good quantum numbers are those associated with the total spin of the system; they take the integer or half-integer values from $|S_A-S_B|$ to S_A+S_B. In most cases, the ground state has the lowest spin $|S_A-S_B|$; the interaction between A and B is antiferromagnetic. In some cases, the ground state has the highest spin S_A+S_B; the interaction is then ferromagnetic. Magnetic susceptibility measurements reveal easily the nature of the interaction. When this interaction is antiferromagnetic, the low-spin ground state is more and more populated as the temperature is lowered, and the product $\chi_M T$, where χ_M is the molar magnetic susceptibility and T the temperature, decreases. When the interaction is ferromagnetic, the high-spin state is more and more populated as T is lowered, and $\chi_M T$ increases. When the interaction occurs between an infinite number of spin carriers instead of only two, in one-, two-, or three-dimensional networks, the problem is obviously more complicated. Three basic situations have to be distinguished: i) If all the spin carriers are identical, and that the interactions between nearest neighbors are antiferromagnetic, $\chi_M T$ decreases and tends to zero as T is lowered. ii) If all the interactions between nearest neighbors are ferromagnetic, whatever the nature of the spin carriers, $\chi_M T$ increases as T is lowered, reaches very high values at low temperature, and eventually may show a maximum due to magnetic saturation effects. iii) If antiferromagnetic interactions occur between two different spin lattices, with $S_A \neq S_B$, the system is said to be ferrimagnetic. In such a case, $\chi_M T$ first decreases as T is lowered, shows a rounded minimum at a finite value, then increases rapidly as T is lowered further. The minimum in the $\chi_M T$ versus T plot is the fingerprint of the ferrimagnetic regime.[6] These three situations are shown schematically in Scheme 1.

Antiferro- or ferromagnetic interactions do not necessarily lead to long-range magnetic ordering. The crucial point is that such a long-range magnetic ordering is strictly impossible for a system consisting of isolated molecules (zero-dimensional), or of isolated chains (one-dimensional). It may occur for a system consisting of isolated layers (two-dimensional), pro-

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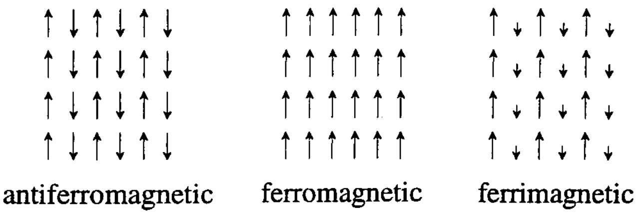


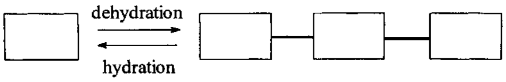
Scheme 1. Antiferromagnetic, ferromagnetic, and ferrimagnetic spin structures.

vided that the spins are not strictly isotropic. On the other hand, long-range magnetic ordering is the normal behavior of a three-dimensional spin network. Therefore, the design of a molecule-based magnet requires one to create interactions along the three directions of space. Furthermore, these interactions must have the good nature, that is they must be either ferromagnetic, or antiferromagnetic between nonequivalent spin lattices.

The interactions between spin carriers may occur through space or through bond. In the former case, we are faced with a genuine molecular lattice with molecules or molecular ions at the lattice points. In the latter case, we are faced with a polymeric or extended structure. Most often the interactions are much stronger when they occur through bonds. This is in particular true when the bridging linkages are conjugated. It follows that an efficient strategy to obtain a molecule-based magnet is to assemble the spin bearing precursors through a polymerization process.

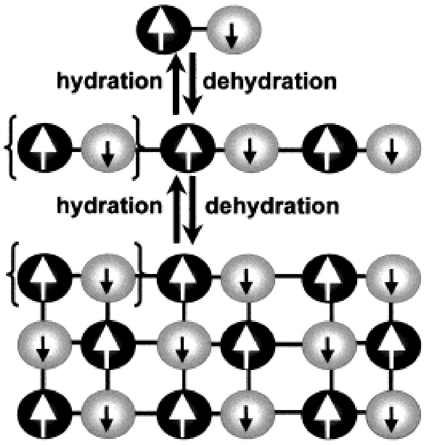
A reversible dehydration–polymerization process

In the last few years, we tested several polymerization processes for assembling spin bearing precursors, and found a very interesting one where polymerization is associated with dehydration.[7] Subsequently, we discovered that this process is entirely reversible. Rehydration of the polymeric network affords isolated precursors, as schematized in Scheme 2.



Scheme 2. A reversible dehydration–polymerization process.

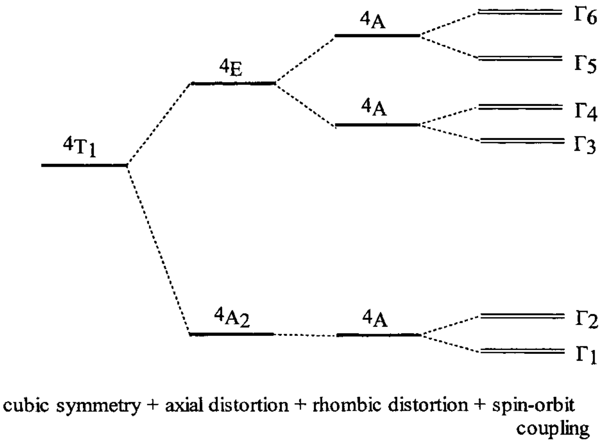
Such a dehydration–polymerization process does not necessarily afford a molecule-based magnet. We have seen that most often the interaction between spin carriers is antiferromagnetic. If it is so, the resulting spin of the polymer is zero. Our strategy to overcome this difficulty was to work with precursors incorporating two different spin carriers, A and B, within the molecular entity, with spins $S_A \neq S_B$; S_A stands for the largest spin and S_B for the smallest one. If the interaction between A and B within the precursor is antiferromagnetic, the ground state spin is $S_A - S_B$, and this ground state spin becomes larger as S_A and S_B become more different. We first developed our approach with Mn^{2+} and Cu^{2+} ions whose spins are $S_{Mn} = 5/2$ and $S_{Cu} = 1/2$. The ground state spin for the AB unit is then $S = 2$. Before polymerization, the intermolecular interactions may be assumed to be negligibly small as compared to the intramolecular A–B interaction. When the precursors are linked to each other, the A–B interaction involving a spin carrier A from a unit and a spin carrier B from an adjacent unit may become rather large, and the resulting ground state spin of the polymer $[AB]_n$, where n is the number of units, is $n(S_A - S_B)$, as schematized in Scheme 3. If n is infinite, and the system is three-dimensional, a long-range magnetic ordering should occur. The system as a whole may be considered as a ferrimagnet. Alternatively, we may say that the $S = 2$ ground state spins of the AB units are ferromagnetically coupled; the strategy would remain valid if the A–B interactions both within the precursor and between adjacent precursors were ferromagnetic. Such a situation, however, is very unlikely. On the other hand, if one of the interactions is ferro- and the other one is antiferromagnetic, then the resulting spin is zero, and no spontaneous magnetization can be expected.



Scheme 3. The dehydration–polymerization process applied to antiferromagnetically coupled heterospin precursors. The process is represented in two steps, which refers to the case of $[CoCu(obbz)(H_2O)_4] \cdot 2H_2O$.

The Co^{2+}–Cu^{2+} case

A very peculiar situation occurs when the A and B spin carriers are Co^{2+} in octahedral environment and Cu^{2+} ions, respectively. The magnetochemistry of Cu^{2+} is straightforward. The spin is $S_{Cu} = 1/2$ whatever the environment, and the $\mathbf{g}_{Cu}$ tensor is somewhat anisotropic with principal values in the 2.0–2.2 range, depending on the structural details. The situation is more complicated for an octahedral Co^{2+} ion. When the actual symmetry is low, which is usually the case in molecular compounds, the combined effect of distortion and spin-orbit coupling most often gives rise to two low-lying Kramers doublets separated by some tens of wavenumbers, as schematized in Scheme 4. The four other Kramers doublets are much higher in energy. [A Kramers doublet is a doubly degenerate state whose degeneracy can only be removed by applying an external magnetic field.] When the temperature is low enough, only the ground Kramers doublet is thermally populated, and the Co^{2+} ion may then be formally treated with



Scheme 4. Energy level spectrum for the Co^{2+} ion in distorted octahedral environment.

an effective spin $S'_{Co} = 1/2$ and a very anisotropic $\mathbf{g}_{Co}$ tensor.[8] The interaction between Co^{2+} and Cu^{2+} gives rise to a nonmagnetic singlet state and a pseudo triplet state, split in zero field. The nonmagnetic state is the lowest in energy if the interaction is antiferromagnetic. The fact that an antiferromagnetically coupled $Co^{2+}Cu^{2+}$ pair has the same ground state as a symmetrical $Cu^{2+}Cu^{2+}$ pair might surprise some readers. Nevertheless, it is so. The two situations, however, are not strictly similar. In the former case, the nonmagnetic ground state may strongly couple with the low-lying excited pseudo triplet state through the Zeeman perturbation. Such a coupling is not possible for the symmetrical $Cu^{2+}Cu^{2+}$ pair. For both pairs, the ground state is nonmagnetic, and $\chi_M T$ tends to zero as T approaches the absolute zero. The profiles of the $\chi_M T$ versus T plots, however, are different. For the symmetrical $Cu^{2+}Cu^{2+}$ pair, the slope of the curve at $T = 0$ is zero; this is not true anymore for the $Co^{2+}Cu^{2+}$ pair (Figure 1). As far as the subject of this concept article is concerned, the important point is that the ground state of an antiferromagnetically coupled $Co^{2+}Cu^{2+}$ unit is nonmagnetic.

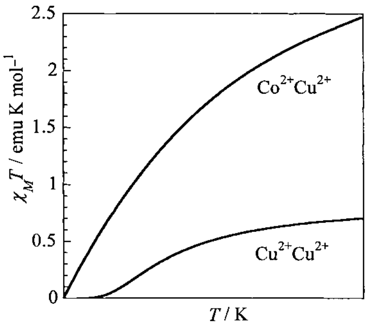


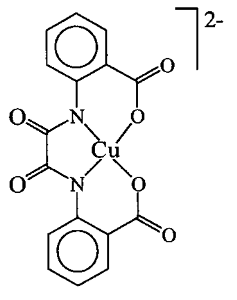
Figure 1. $\chi_M T$ versus T plots for antiferromagnetically coupled $Co^{2+}Cu^{2+}$ and $Cu^{2+}Cu^{2+}$ pairs.

Let us now link together the $Co^{2+}Cu^{2+}$ units through the dehydration–polymerization process presented above, and look for the ground state of the extended system. At first sight, one could think that linking together units with a nonmagnetic ground state should result in a nonmagnetic extended system. This is not true. In the low-temperature range, the Co^{2+} ion carries a magnetic moment $g_{Co}\beta S'_{Co}$. Not only is this magnetic moment very anisotropic due to the anisotropy of the $\mathbf{g}_{Co}$ tensor, but it is not compensated by the $g_{Cu}\beta S_{Cu}$ magnetic moment carried by the Cu^{2+} ion. As a matter of fact, the average value of g_{Co} is much higher than that of g_{Cu}. In an extended system, this noncompensation of the local moments results in ferrimagnetic behavior, with $\chi_M T$ showing a minimum at a certain temperature and increasing very rapidly as T is lowered further below this temperature.[9] If the extended network is three-dimensional, a long-range magnetic ordering together with a spontaneous magnetization should occur. Owing to the magnetic anisotropy of Co^{2+} (vide infra), a long-range ordering may also be expected for a two-dimensional network.

To sum up, the ground state of an isolated $Co^{2+}Cu^{2+}$ unit is nonmagnetic, with $\chi_M T = 0$ at the absolute zero, provided that the interaction is antiferromagnetic. If such $Co^{2+}Cu^{2+}$ units are linked together in a two- or three-dimensional network with antiferromagnetic Co^{2+}–Cu^{2+} interactions between the units, then the ground state becomes a ferrimagnetic state. The system is a magnet. Furthermore, this magnet may be anticipated to exhibit a strong coercivity. As a matter of fact, the coercivity of a magnet which confers a memory effect on the material is governed by both physical and chemical factors. The main physical factors are the size and shape of the particles. The key chemical factor is the magnetic anisotropy of the spin carriers. The Co^{2+} ion in distorted octahedral environment is the most anisotropic 3d ion, and to date the strongest coercive fields for molecule-based magnets have been found in Co^{2+} containing compounds.[10, 11]

The molecular magnetic sponge $[CoCu(obbz)] \cdot n H_2O$

The $[CoCu(obbz)(H_2O)_4] \cdot 2H_2O$ starting material: All the concepts presented above apply to the compound $[CoCu(obbz)(H_2O)_4] \cdot 2H_2O$ and its dehydrated derivatives; obbz stands for *N*,*N*′-bis(2-carboxyphenyl)oxamido.[12] This compound was obtained through the reaction of the dianion $[Cu(obbz)]^{2-}$ with Co^{2+}. Its structure consists of neutral $[CoCu(obbz)(H_2O)_4]$ units, as shown in Figure 2, and noncoordinated water molecules. The two oxamido and two carboxylato oxygen atoms of $[Cu(obbz)]^{2-}$ are potentially coordinating. In fact, only the oxamido oxygen atoms are bound to Co^{2+} in $[CoCu(obbz)(H_2O)_4]$. The carboxylato oxygen atoms remain free. Co^{2+} is in an octahedral environment with four water molecules in its coordination sphere, and Cu^{2+} is in a square-planar environment.



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

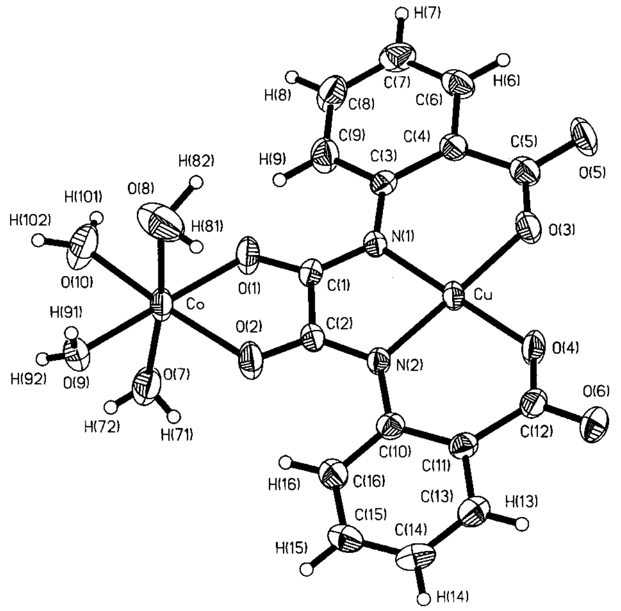


Figure 2. Molecular structure of $[CoCu(obbz)(H_2O)_4]\cdot 2H_2O$.

The temperature dependence of $\chi_M T$ for $[CoCu(obbz)(H_2O)_4]\cdot 2H_2O$ (Figure 3 top) is typical of an antiferromagnetically coupled $Co^{2+}Cu^{2+}$ pair. $\chi_M T$ tends to zero as T is lowered down the absolute zero; as anticipated, the ground state is nonmagnetic.

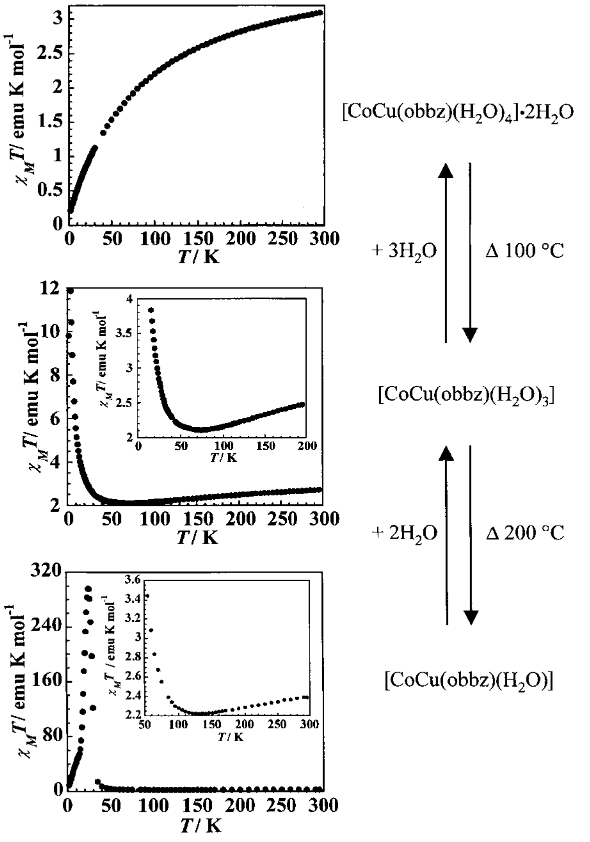


Figure 3. Temperature dependences of $\chi_M T$ for $[CoCu(obbz)(H_2O)_4]\cdot 2H_2O$ (top), $[CoCu(obbz)(H_2O)_3]$ (middle), and $[CoCu(obbz)(H_2O)]$ (bottom). The inserts emphasize the minima in the curves, charateristic of the ferrimagnetic regime. Note the different scales of $\chi_M T$ values for the three curves.

$[CoCu(obbz)(H_2O)_3]$ and $[CoCu(obbz)(H_2O)]$: Thermogravimetric studies reveal that the starting material can be dehydrated to give two well-defined new compounds. At about 100 °C, the two noncoordinated water molecules along with one of the water molecules bound to Co^{2+} are released to give the compound $[CoCu(obbz)(H_2O)_3]$. Heating this compound up to about 200 °C results in the release of two more water molecules to give $[CoCu(obbz)(H_2O)]$ (Figure 3). This dehydration process is perfectly reversible. If a sample of $[CoCu(obbz)(H_2O)]$ is maintained at room temperature in the close vicinity of a source of water, the rehydration is complete; it affords a material whose chemical composition, structure as revealed by X-ray diffraction, and physical properties are strictly identical to those of the starting material. The dehydration–rehydration cycle can be repeated as many times as desired without any degradation of the material, provided that the temperature never exceeds 275 °C.

The magnetic properties of both the tri- and monohydrate are totally different from those of the starting material. The $\chi_M T$ versus T plot for $[CoCu(obbz)(H_2O)_3]$ (Figure 3 middle) is typical of a ferrimagnetic behavior with a minimum of $\chi_M T$ at 74 K. $[CoCu(obbz)(H_2O)_3]$ has an extended structure with two sublattices of magnetic moments which do not compensate. This compound, however, presents no long-range magnetic ordering down to 2 K, which strongly suggests that its structure is one-dimensional. In fact, two chain compounds of the same kind have been structurally characterized. In one of them, Co^{2+} is replaced by Mn^{2+}. Its formula is $[MnCu(obbz)(H_2O)_3]$.[13] In the other, obbz is replaced by obp (obp = *N*,*N'*-bis(2-carboxyethyl)oxamido).[14] The cobalt atom is surrounded by six oxygen atoms, two of which come from the oxamido group, three from water molecules, and the sixth from the carboxylato group of a neighboring unit. Most likely, $[CoCu(obbz)(H_2O)_3]$ possesses a similar structure (Figure 4). Infrared and Raman data support this assumption.

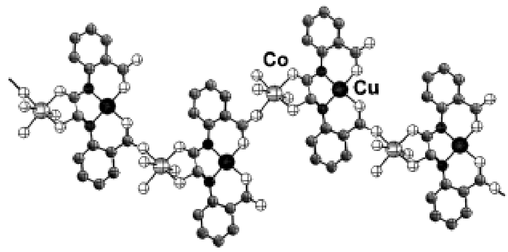


Figure 4. Probable chain structure for $[CoCu(obbz)(H_2O)_3]$.

The $\chi_M T$ versus T plot for $[CoCu(obbz)(H_2O)]$ (Figure 3 bottom) again reveals a ferrimagnetic behavior, with a minimum of $\chi_M T$ at 130 K. As the temperature is lowered further below 130 K, $\chi_M T$ increases very abruptly, and reaches very high values before reaching a maximum around 25 K. The decrease of $\chi_M T$ below 25 K is due to saturation effects. Such a curve strongly suggests that a long-range magnetic ordering occurs. The onset of a magnetic transition is confirmed by the temperature dependence of the field-cooled magnetization (FCM), zero-field-cooled magnetization (ZFCM), and remnant magnetization (REM) (Figure 5). The FCM, measured by cooling the sample under a field of 1 Oe, presents a break around 30 K. The critical temperature,

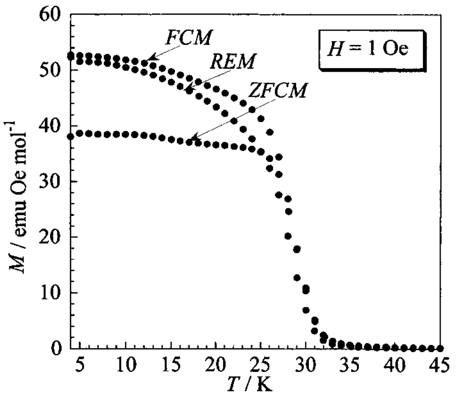


Figure 5. Temperature dependences of the field-cooled magnetization (FCM), zero-field-cooled magnetization (ZFCM), and remnant magnetization (REM) for [CoCu(obbz)(H_2O)].

determined as the inflexion point of the FCM = f(T) curve, is found as $T_c = 30$ K. The ZFCM, measured by cooling the sample in zero field, then warming up under a field of 1 Oe, is lower than the FCM at all temperatures below T_c. This is because the temperature is too low to allow the domain walls to move freely. The ZFCM merges with the FCM at T_c. Finally, the REM, obtained by cooling the sample under the field, then warming up in zero field, vanishes at T_c.

Further information may be deduced from ac magnetic measurements. Perhaps, some readers are not familiar with such measurements, and we would like to provide some information before presenting the results.[15] In dc (direct current) measurements, a static magnetic field H is applied, which induces a magnetization M. The dc susceptibility, χ_M, is then defined as dM/dH. For paramagnetic species, the $M =$ f(H) curve is linear as long as the field is not too strong and the temperature is not too low. It follows that the susceptibility may be expressed as M/H. In ac (alternating current) measurements, an oscillating field of the form $H_0 + h\exp(i\omega t)$ is applied, where H_0 is the static field, which may be taken as zero, h is the amplitude of the oscillating field, ω its frequency, and t the time. The ac susceptibility, χ_{ac}, is then equal to dM/dH. This ac magnetic susceptibility is determined from its two components, the in-phase (or real) component, χ', and the out-of-phase (or imaginary) component, χ''. The in-phase susceptibility is an initial susceptibility with the same phase as the oscillating field. The out-of-phase susceptibility is related to the phase delay of the magnetization with respect to the oscillating field in the magnetically ordered phase. The presence of a non-zero χ'' response characterizes a magnet.

The in-phase, χ', and out-of-phase, χ'', ac molar magnetic susceptibilities with a zero static field for [CoCu(obbz)(H_2O)] are displayed in Figure 6. χ'' is not zero below 31 K, which is in line with the onset of a magnetic transition. Both χ' and χ'' present a peak, at 27 and 25 K, respectively. Interestingly, the temperatures of the maxima do not depend on the frequency ω up to 10^3 Hz ; the material is a genuine magnet, and not a spin glass or a superparamagnet.

Not only [CoCu(obbz)(H_2O)] is a magnet, but it is a hard magnet. The field dependence of the magnetization at 5 K (Figure 7) reveals a well-shaped hysteresis loop, with a coercive field of 3 kOe.

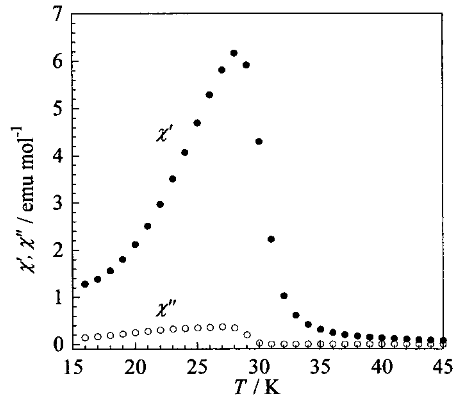


Figure 6. Temperature dependences of the in-phase, χ', and out-of-phase, χ'', ac magnetic susceptibilities for [CoCu(obbz)(H_2O)].

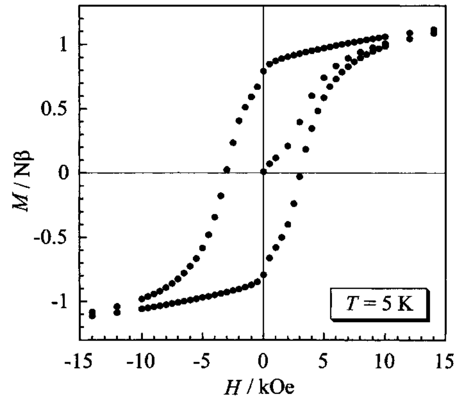


Figure 7. Field dependence of the magnetization and hysteresis loop at 5 K for [CoCu(obbz)(H_2O)].

The magnetic properties reported above for [CoCu(obbz)(H_2O)] are only compatible with a two- or three-dimensional structure, with octahedral Co^{2+} ions. A two-dimensional structure can be achieved if the two water molecules which are released when passing from [CoCu(obbz)(H_2O)$_3$] to [CoCu(obbz)(H_2O)] are replaced by two carboxylato oxygen atoms belonging to two neighboring chains (Figure 8). It should be noted that, if the Co^{2+} ion was in a tetrahedral environment, its magnetic anisotropy would be much less pronounced, and the coercive field would definitely not reach a value as high as 3 kOe.

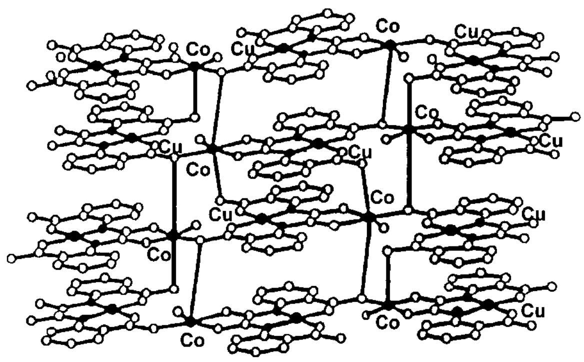
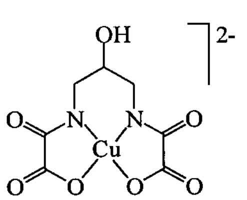


Figure 8. Possible association of chains in [CoCu(obbz)(H_2O)], affording a two-dimensional structure. For clarity, the apical Co–O(caboxylato) bonds have been lengthened.

Some other sponges

Quite a few other molecule-based magnets were obtained through reversible dehydration of paramagnetic (or sometime antiferromagnetic) species. The very first example is $[MnCu(obbz)]\cdot nH_2O$ with $n = 5$ or 1.[16] The pentahydrate has a chain structure similar to that shown in Figure 4 and displays ferrimagnetic behavior. Due to very weak interchain interactions, the compound exhibits a long-range antiferromagnetic transition at 2.3 K. When four out of five water molecules are released, the same association of chains as described in the previous section happens, and the monohydrate is a genuine magnet with $T_c = 14$ K. The process is again reversible. Another example of a magnetic molecular sponge in $Mn^{2+}Cu^{2+}$ compounds is provided by $[MnCu(pbaOH)]\cdot nH_2O$ synthesized from the $[Cu(pbaOH)]^{2-}$ anion. The pentahydrate (whose correct formula is $[MnCu(pbaOH)(H_2O)_3]\cdot 2H_2O$) has a chain structure with an alternation of Mn^{2+} and Cu^{2+} ions bridged by oxamato bridges. The interchain interactions are very weakly antiferromagnetic, and the material presents a three-dimensional ordering of the ferrimagnetic chains at $T_c = 2.4$ K. A field of 0.9 kOe is sufficient to overcome these interchain interactions, so that the compound may be described as a metamagnet built from ferrimagnetic chains.[17] If the two noncoordinated water molecules are released, the interchain interactions become ferromagnetic, and the compound is a magnet with $T_c = 4.6$ K.[4, 5] Removing the water molecule weakly bound to the Cu atom in the apical position results in an increase of T_c up to 30 K.[18] If Mn^{2+} is replaced by Co^{2+}, we are again faced with a magnetic sponge.[19] The pentahydrate $[CoCu(pbaOH)(H_2O)_3]\cdot 2H_2O$ is a chain compound in which the ferrimagnetic chains interact antiferromagnetically within the lattice. Removing the two noncoordinated water molecules through a thermal treatment results in the new chain compound $[CoCu(pbaOH)(H_2O)_3]$ which exhibits a ferromagnetic ordering of the ferrimagnetic chains at $T_c = 9.5$ K. Removing a third water molecule, occupying the apical position in the copper coordination sphere results in $[CoCu(pbaOH)(H_2O)_2]$ which again presents a long-range ordering, but at $T_c = 38$ K. This magnet is very hard. Its coercive field at 2 K is 5.66 kOe.



Other examples of stabilization of a ferromagnetic state through partial dehydration have been described.[20–22] The case of $[CoCu(obbz)]\cdot nH_2O$, however, remains particularly spectacular as the reversible dehydration leads from a system with a nonmagnetic ground state to a hard magnet.

Conclusion

Some molecular compounds behave as sponges. They can reversibly release and reabsorb water molecules, both noncoordinated and coordinated, a process which is accompanied by a dramatic change of magnetic properties. If we focus on compounds such as $[CoCu(obbz)]\cdot nH_20$, we may describe the situation as follows: when the sponges are hydrated, or wet, they exhibit a nonmagnetic ground state. When they are dehydrated, or dry, they are hard magnets with a strong coercive field. What is quite remarkable is the reversibility of the process. This reversibility is a well-known phenomenon for the lattice water molecules; it occurs in many hydrates. On the other hand, the reversible release of coordinated water molecules, accompanied by a polymerization process, to our knowledge, was not documented. The Co–O bonds can be broken and created without destroying the chemical essence of the objects. On the other hand, the architecture as a whole is strongly modified. Dehydration increases the structural and magnetic dimensionality from 0 (isolated molecules) to 2 or 3; rehydration decreases this dimensionality.

Is it possible to analyze further why such a reversible dehydration–rehydation process may occur? Let us first point out that in the lattice of the hydrated compound, for instance $[CoCu(obbz)(H_2O)_4]\cdot 2H_2O$, the shortest intermolecular metal–metal separation is between Co and Cu. Moreover, this separation is shorter than the intramolecular one, 5.109 versus 5.295 Å. Furthermore, the molecules are connected through an extensive network of hydrogen bonds involving a coordinated water molecule in one molecule and carboxylate groups of a neighboring molecule (Figure 9). In a certain sense, the molecular lattice is pre-formed to permit the equilibrium of Scheme 5. Under experimental conditions favoring the release of water molecules (vacuum or heating), this equilibrium is displaced toward the right-hand side. In the presence of an excess of water, it is displaced toward the left-hand side. This equilibrium is very complex; it involves a step occurring in the solid state, the creation/breaking of the Co–carboxylato bonds, as well as a step occurring in a solid–liquid heterogeneous phase, the breaking/creation of the Co–water bonds.

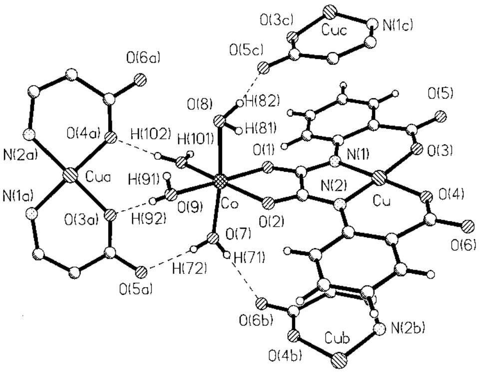
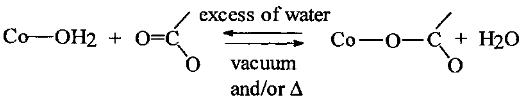


Figure 9. Hydrogen bond network for $[CoCu(obbz)(H_2O)_4]\cdot 2H_2O$.



$$\text{Co—OH}_2 + \text{O=C}\overset{/}{\underset{\backslash\,\text{O}}{}} \underset{\substack{\text{vacuum}\\ \text{and/or }\Delta}}{\overset{\text{excess of water}}{\rightleftharpoons}} \text{Co—O—C}\overset{/}{\underset{\backslash\,\text{O}}{}} + \text{H}_2\text{O}$$

Scheme 5. Reservible breaking and formation of $Co–OH_2$ bond.

One of the most appealing facets of the field of molecular materials resides in the possibility of combining some physical properties which are encountered in classical materials together with some other properties specific to the molecular state. The molecular magnetic sponges illustrate this situation. Solid-state chemistry provides nonmagnetic materials as well as magnets, but no material for which one can pass reversibly from a nonmagnetic state to a magnetically ordered state through a simple chemical process such as dehydration–rehydration. Molecular chemistry can provide such exotic materials, owing to the remarkable softness of the molecular crystal lattices.

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[1] See, for instance, *Proceedings of the Fifth International Conference on Molecule-Based Magnets, Mol. Cryst. Liq. Cryst.* (Eds.: K. Itoh, J. S. Miller, K. Takui), *vol. 305–306*, **1997**.

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