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Abstract. — The capacity of hydrogen bonds as crystalline design elements for the preparation of solid state supramolecular organizations with relevant magnetic properties is reviewed. It will be shown here that hydrogen bonds fulfill two distinct purposes. One function is a structural one through which is possible to control up to certain level the relative arrangements of radical molecules. The other role of hydrogen bonds is a magnetic one since these bonds introduce proper pathways for the transmission of intermolecular magnetic interactions. Using this methodological approach several molecular magnetic solids have been prepared with hydroxylated phenyl α-nitronyl nitrooxide radicals. These molecular solids are formed by supramolecular motifs (dimers, chains, and planes) bonded by strong hydrogen bonds which are linked to each other by other weak forces that form the rest of the crystals. Consequently, the solids show different structural dimensionalities that in some cases do not agree with the magnetic ones. Accordingly with such distinct structural and magnetic dimensionalities, the resulting molecular solids show a wide variety of magnetic behaviors. Remarkable are the purely organic 2-D and 3-D ferromagnets reported here. Finally, the most relevant mechanisms explaining intermolecular magnetic interactions as well as the most promising applications expected for purely organic magnets are also included.

1. Introduction

Since the discovery of the first example of a purely organic ferromagnet, several other interesting organic magnetic materials have been obtained and studied in detail [1,2]. The enormous interest that these kind of novel materials motivate in the scientific community lies on the new and unexpected properties that they might exhibit. In this sense, the combination of a macroscopic magnetic property, like the superparamagnetic and ferromagnetic, and the intrinsic properties of organic compounds might open the way to a new and fascinating world of advanced materials. Some of the foreseeable advantages of organic materials over the traditional inorganic

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ones have been discussed elsewhere [3]. They might become superior to traditional magnets as far as applications involving light absorption and reflection are concerned. In fact, organic compounds are usually transparent in many spectral regions and could be in principle obtained in optically active chiral forms. Thus, they might be used as magneto-optical switches and for the manipulation of polarized light in optical devices if Faraday and Kerr effects are exploited. Organic materials are generally electric insulators, so they might lead to insulating magnets in contrast with most of the traditional magnets that are electric conductors being, therefore, good candidates for electromagnetic shielding purposes. Plasticity, flexibility and solubility in common organic solvents are general characteristics of organic compounds that confer them an easy processability. Hereby, organic magnets are ideal candidates to obtain magnetically active thin films and colloidal dispersions with ferrofluid properties. Biocompatibility is another characteristic of organic compounds that permits to imagine biomedical applications like for instance the use of organic magnets or high-spin molecules for drug addressing and as selective contrasting agents in nuclear magnetic resonance imaging. Finally, the state-of-the-art of organic chemistry techniques permits nowadays to synthesize tailor-made compounds and, therefore, to perform small structural modifications in order to tune their physical properties. Such a tunability is unprecedented in most of traditional inorganic materials and, consequently, opens a wide range of practical opportunities.

From the perspectives already mentioned it is clear the enormous interest existing nowadays for this kind of magnetic materials. However, as we will see latter, the design and synthesis of purely organic ferromagnetic materials is not a simple and direct task. Many years are still required for any practical application. Such materials require three major electronic and structural prerequisites: 1) presence of permanent magnetic moments in their building blocks; i.e., the use of repeating units with electronic open-shell character and high enough persistence; 2) settlement of proper magnetic interactions between these permanent magnetic moments in order to align them parallel with respect to each other; i.e., the establishment of ferromagnetic interactions; 3) arrangement of such interacting permanent magnetic moments over large and three (or two) dimensional regions (domains) of the material. The problems associated with all these three steps are by no means simple because organic species containing unpaired electrons usually tend to be rather unstable and, further, whenever they are bonded or they come close enough to interact with each other they tend to pair antiparallel their spins. Nevertheless, several efficient strategies have been already developed in order to tackle both problems. Thus, different ways to increase the chemical and thermal stabilities of open-shell compounds (free radicals and ion-radicals, etc.) have been reported and, therefore, these persistent species could be used as open-shell repeating units. Similarly, different strategies that guarantee the ferromagnetic couplings among neighboring open-shell species have been reported [4]. Consequently, the most problematic step in the preparation of an organic magnet is the extension of the ferromagnetic couplings among the neighboring open-shell units into the three (or two) dimensions of the material. In fact, a precise control of connectivities, conformations, and the relative spatial orientations of the repeating units in the organic material is crucial to achieve such a goal. Hence, the challenge to the synthetic chemistry to solve these supramolecular problems is formidable; but we believe that this field will benefit from the rapid advances of the Supramolecular Chemistry.

According to the nature of the materials and the type of ferromagnetic coupling mechanisms involved, two different approaches have been followed in order to prepare organic ferromagnets [1]: (i) Polymeric Materials, in which the magnetic interactions between open-shell monomer repeating units are transmitted through covalent skeletons, and (ii) Molecular Solids, in which the ferromagnetic couplings among open-shell molecules are transmitted through the space or non covalent bonds.
In the following we will review the main achievements with the last kind of crystalline materials paying a special attention to the results obtained with the family of \( \alpha \)-nitronyl nitroxide radicals 1; in particular with those radicals substituted with hydroxylated phenyl groups. This family of hydroxylated radicals have permitted to show that hydrogen bonds are able to link properly the molecules and at the same time to establish proper pathways to transmit the magnetic interactions yielding relevant macroscopic magnetic properties. This methodological approach was inspired on the previous work of Awaga et al. [5] using Coulombic forces instead of hydrogen bonds. We believe that the methodological approach here described in detail is representative of present trends that are followed in order to obtain organic/molecular materials with relevant magnetic properties.

![Diagram](image)

2. Magnetic Interactions in Molecular Solids

Generally speaking, a macroscopic physical property of an organic molecular solid, like magnetism, is always related to the relative arrangement of its constituent building blocks since such layouts control the intermolecular electronic interactions among these units which are the ultimately responsible for their macroscopic magnetic properties. Accordingly, there is a great need to control these structural characteristics in order to rule the magnetic behavior of the material. It is well known that the relative molecular arrangements in crystalline organic molecular solids are a consequence of several structural factors and numerous subtle intermolecular forces [6]. Coulombic attractive forces, hydrogen bonds [7], \( \pi - \pi \) stacking and van der Waals forces are the most often used pulling forces in the attempts to direct the packing of a given purely organic molecular material. Nevertheless, there is still a long way to go in order to produce tailor-made molecular solids: \textit{i.e.} designed crystalline materials with predefined structures and properties. The main reason for this difficulty is the fact that the way molecules arrange in a crystal is not at all easy to predict [8]. Only in the most favorable cases some crystalline features or motifs can be concluded \textit{a priori} from the molecular geometry and connectivity. The overall crystal packing remains a largely unknown variable until it is experimentally determined. In consequence, neither the crystal packing nor the electronic intermolecular interactions of a new material can at all be predicted \textit{a priori}. Thus, it is obvious that the establishment of new methodologies for designing crystal structures is indispensable in this field.

Purely organic magnetic materials, and in particular substituted \( \alpha \)-nitronyl nitroxide radicals 1, have been studied during the last decade almost exclusively in the solid state [9]. Most probably, the driving force for most of such studies was the discovery of the first example of purely organic ferromagnet [2] and the relevant magnetic properties that have several of their metal transition complexes [10]. Nevertheless, this family of radicals exhibit many other interesting properties that are not restricted to the solid state and that were extensively studied since Ullman and coworkers synthesized for the first time an \( \alpha \)-nitronyl nitroxide radical in 1968 [11].
The geometry constraints for magnetically active organic molecules, like free radicals or radical ions, are by far more complex than the highly symmetric structures of inorganic metal ions. In consequence, the relationship between relative molecular arrangements and magnetic interactions is less evident, and probably can not be established as clearly as it can for inorganic compounds. Nevertheless, we believe that there is a methodological approach for designing crystal structures showing controlled magnetic properties. This methodological approach can be divided into the following two steps: The first one implies the use of a *supramolecular design element* or *tool* capable to link molecules together in a predetermined manner. This tool should be a suitable driving force, that forces the molecules to lay out in a highly directional way with respect to each other. Coulombic forces in charged molecules, hydrogen bonds, the intelligent use of steric hindrances [12], or the combination of these or other tools may fulfill the desired target providing excellent opportunities for controlling the relative arrangement of molecules. The second step is to test if the achieved relative arrangements between molecules are able to induce a ferro- or an antiferromagnetic interaction and to determine the intensity of such a magnetic exchange. In order to accomplish both steps, a series of compounds with several structural and electronic requirements should be synthesized. This series of compounds will permit magneto-structural correlations, and from these, new tailor-made compounds might be synthesized.

Before going ahead with this methodological approach, a brief review of the most widely accepted mechanism that explains the magnetic interactions in magnetic molecular solids, the so known McConnell I mechanism, is given here [13]. This mechanism was proposed in the earlier sixties by McConnell and permits the prediction of the sign of the exchange interaction between two free electrons belonging to two neighboring open-shell molecules arranged in a given way. All the atoms of a free radical bear a certain amount of the so called *spin density* that primarily reflects the distribution of the unpaired electron all over the molecule. The spin density on a certain atom can be positive or negative depending on the particular electronic structure of the studied molecule. Specifically, as a result of the spin polarization mechanism, negative spin density can appear on some atoms. Simply speaking, the McConnell I mechanism states that if the atoms of both molecules that are closest one to each other, having the most significant overlap, bear the same sign of the spin density the resulting magnetic interaction between both molecules will be antiferromagnetic. By contrast, the interaction will be ferromagnetic if the sign of the overlapping spin densities is different. It can be imagined that in the regions in which there is a direct overlap of the molecular orbitals, the same phenomenon that in the formation of a covalent bond occurs; i.e., the spins of the two involved non paired electrons in the spatial areas with most overlap should be of opposite sign. The validity of this quite simple model was experimentally confirmed several years later by Iwamura *et al.* [14] using the three different isomers of the bis(phenylmethylenyl)[2.2]paracyclophane. EPR spectroscopy revealed that the quintet state was the ground state of the *pseudo-ortho* and *pseudo-para* isomers of these biscarbene derivatives, while the singlet state was the ground state for the *pseudo-meta* isomer. Results that are in accordance with theoretical predictions based on the signs of the overlapping spin densities of the two interacting carbene moieties of each isomer.

In addition to the mentioned mechanism it is important to stress another interesting situation that is also based on the Pauli exclusion principle and has also important consequences in *Molecular Magnetism*. Thus, it is predicted that when the overlap between the orbitals carrying the lone electron is strong and adopt an orthogonal disposition, a ferromagnetic interaction is most favored [15]. In short, such ferromagnetic interactions appear when a maximum overlap between the spin carrying orbitals occurs and at the same time the orbital overlap integral
should tend to be almost zero. Under such conditions the electronic repulsion tend to align the spins in a parallel fashion.

3. Hydrogen Bonds as Structural and Magnetic Design Elements

It is very well known that hydrogen bonds act as a very directional force giving rise to well defined supramolecular patterns of molecules [16]. Consequently, these kind of bonds are often used in order to control the relative disposition of neighboring molecules in the solid state as well as in solution. A lot of work has been done in the study of the hydrogen bond itself by means of surveys and correlations with the Cambridge Structural Database [17] or also in the study of the formation of aggregates of molecules linked together through hydrogen bonds [18].

The extreme importance of the studies on these intermolecular forces can easily be understood by realizing that most of the biological macromolecules (peptides, enzymes, etc.) and processes (DNA replication, enzyme activity, etc.) are mainly controlled by hydrogen bonds.

Hydrogen bonds are known to be a non-covalent bonding interaction being basically electrostatic in its nature. For this reason, an explanation of its characteristics can reasonable be achieved by studying the electrostatic potential maps of the involved molecules. For this purpose, two equipotential surfaces are drawn around the isolated molecule, one with positive and the other with negative potentials. The analysis of the shape and the self-complementary of both equipotential surfaces provides an idea about the expected relative spatial orientation of hydrogen bonded molecules. In the frame of Molecular Magnetism, hydrogen bonds linking together spin carrying units, either metal ions or radical molecules, have some characteristics that make them very interesting in order to control the intermolecular magnetic interactions. On one hand, the relative disposition of hydrogen bonded molecules is expected to have a restricted degree of freedom due to the high directionality of the hydrogen bonds. On the other hand, hydrogen bonds usually result in very short intermolecular distances between the two interacting sites of neighboring molecules. In consequence, specific magnetic interactions can appear between the hydrogen bonded spin carrying units being furthermore such intermolecular magnetic interactions controllable with organic chemistry synthetic techniques. Some examples are found in the literature where hydrogen bonds have been used and studied as transmitters of magnetic interactions in metal ions salts [19]. In these compounds water molecules act as a bonding unit between different metal ions and have actually proved to transmit magnetic interactions effectively between the metal centers. By contrast, no systematic study has been carried out concerning the role of hydrogen bonds in the magnetic transmission in purely organic magnetic materials.

4. Structural and Electronic Characteristics of Hydroxylated Phenyl α-Nitronyl Nitroxide Radicals

A family of open-shell compounds suitable to perform such a study with hydrogen bonds is the hydroxylated phenyl α-nitronyl nitroxide radicals. The aforementioned radicals have in common the following structural and electronic characteristics. On one hand, they have an heterocyclic imidazolyl-1-oxy-3-oxide ring — the α-nitronyl nitroxide ring — in which most of the spin density is located. On the other hand, they are built up by a second ring, in this case an aromatic phenyl ring, that can be substituted in different positions by one, two, or more hydroxy groups. Moreover, it is known that a certain amount of spin density is situated on this second aromatic ring due to a spin polarization mechanism that transmits some spin density and at the same time induces an alternation of their signs on these aromatic atoms. Different experimental results have confirmed such electronic characteristics [20]. But by far
the most interesting feature of this family of compounds is the simultaneous presence of OH
and NO groups in each molecule. Semi-empirical and \textit{ab-initio} computations performed with
these radicals show that the mentioned groups are suitable to act as hydrogen bond donor and
acceptor groups, respectively [21]. Accordingly, these functional groups are expected to favor
the establishment of strong hydrogen bonds of the O-H $\cdots$ O-N type inducing interesting close
contacts between certain spatial regions of the involved molecules. In a normal hydrogen bond
the O $\cdots$ O distance lies around 2.5 - 2.9 Å [22], and, therefore, these quite short intermolecular
distances can be expected to have a relevant magnetic importance because one of the involved
groups (the NO moiety) carries a large amount of the spin density.

A closer structural analysis shows that the magnetic interactions that are established be-
tween hydrogen bonded compounds can be explained by using the above mentioned McConnell
I mechanism. For this purpose, it is convenient to draw and discuss briefly the spin density
distribution map of phenyl \(\alpha\)-nitronyl nitroxide radical, depicted in Figure 1. This map de-
picts the main features of the distribution of the lone electron around this nitronyl nitroxide
radical, as extracted from polarized neutron diffraction experiments [23], NMR data [24], and
semi-empirical and \textit{ab-initio} calculations [25]. No significant differences in the spin density
distribution are observed depending on the aromatic substitution, as revealed by solution EPR
spectra of different radicals [26]. Thus, for the present family of compounds the main spin
density lies equally distributed on both NO groups, while the bridgehead carbon atom bears a
quite large negative spin density. In the aromatic ring, the spin densities alternate in sign being
positive on the \textit{ipsos} and \textit{meta} carbon atoms and negative on the \textit{ortho} and \textit{para} ones. The spin
densities on the aromatic hydrogen atoms and the oxygen atoms have opposite sign than that
found on the carbon atoms they are linked to. It is expected that the hydroxylic hydrogen atom
bears an extremely small spin density that can not even be detected by EPR but, following
the alternation rule, its sign is supposed to be the contrary to those found on its neighboring
oxygen atom. Spin densities on hydrogen atoms of the CH$_3$ groups were experimentally found
to have a small but always negative values [21,24,26].

In consequence, this simple picture predicts that in case of an intermolecular O-H $\cdots$ O-N
hydrogen bond involving the \textit{ortho} or \textit{para} hydroxy groups, that have a negative spin density
on their hydrogen atom, a weak ferromagnetic coupling, if any, will be favored due to the
close contact of nuclei with opposite spin density signs. On the other hand, in the case of an
O-H $\cdots$ O-N hydrogen bond involving the \textit{meta} hydroxy group, two atoms of the same sign
of spin density will be very close and one would expect weak antiferromagnetic interactions.
Finally, close contacts produced by weak C-H $\cdots$ O-N hydrogen bonds between CH$_3$ and NO
groups are also expected to induce intermolecular ferromagnetic interactions due to the op-
posite signs of the spin densities on the involved nuclei. In addition, hydrogen bonds would

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\textbf{Fig. 1.} — Schematic view of the spin density distribution of phenyl \(\alpha\)-nitronyl nitroxide radical.
also have indirect consequences on the magnetic properties of bonded radicals. Probably the
most important one would occur when these bonds approach two NO groups of neighboring
molecules. In such a situation two molecular regions with very large and positive spin densi-
ties would be close, favoring a strong antiferromagnetic interaction. Keeping in mind all the
simple rules and ideas outlined above, we will try to interpret and correlate the experimental
results found with six members of the hydroxylated phenyl α-nitronyl nitroxide radical family
depicted below, radicals 2-7.

![Chemical structures](image)

After describing the synthesis and crystal structure of each of them, an interpretation of
their macroscopic magnetic properties using the aforementioned ideas will be done. From
this magneto-structural correlation it will be shown that the hydrogen bonds really fulfill two
purposes, namely the control of the relative arrangement of radicals, at least up to a certain
level, and the introduction of a proper pathway for the transmission of the magnetic interactions
that can be appropriately explained with the McConnell I mechanism.

5. Hydrogen bonded Supramolecular Organizations of Hydroxylated Radicals with
Relevant Magnetic Properties

All the compounds were synthesized following the multi-step procedure described by Ullman
et al. [11] with minor modifications. The radicals were characterized by means of spectroscopic
techniques and elemental analysis. Single crystals suitable for X-ray diffraction and anisotropy
EPR studies were obtained by slow evaporation from saturated solutions of radicals in toluene,
heptane or other organic solvents. For other physical measurements, like magnetic suscepti-
bility or muon spin rotation experiments, polycrystalline samples were used. The crystalline
purity of these samples were always checked by their powder X-ray diffraction patterns.

5.1. Crystalline Packings of Hydroxylated Radicals. — In the analysis of the present
crystal structures we can observe, as expected, that the hydrogen bonds play a crucial role in
the determination of the crystal packing. For the sake of systematization we will describe the observed crystalline motifs using a nomenclature similar to that used in biological systems. With primary structure we refer to the covalent structure of the molecules itself. By contrast, with secondary structure we define the motif that is obtained through the linkage of molecules via strong hydrogen bonds of N-O···H-O and/or C-O···H-O types. Depending on the propagation of such strong hydrogen bonds along the whole crystal, such motifs can have different dimensionalities that range from 0-D (dimers) to 2-D (molecular planes). As tertiary structure we describe the assembly of secondary structures linked together through weak hydrogen bonds either N-O···H-C and/or C-O···H-C types that are established between the NO groups and hydrogen atoms of the aromatic rings or the methyl groups. Finally, as quaternary structure we refer the whole structure of the crystal that is joined by other weak forces, like van der Waals, $\pi - \pi$ interactions, etc. As main conclusions of this analysis we will see that the crystalline motifs of the secondary structures are quite easily predictable from the electrostatic potential maps and by the usual considerations of molecular design. On the other hand, although they can be rationalized once they are known, tertiary structures can not a priori be predicted. By contrast, the quaternary structures are non predictable for the present time, as also occur for other organic compounds. Another interesting point is that molecular solids show structural dimensionalities that not always agree with the magnetic ones.

5.1.1. Detailed Crystalline Structural Analyses. — Radical 2 has a OH group in the meta position of the aromatic ring and, therefore, there is a hydrogen bond acceptor (NO) and donor (OH) on the same side of the molecule. In accordance with this primary structure, the analysis of the electrostatic potential map of this compound shows clearly two regions with negative and two other regions with positive potentials on the side of the molecule in which the OH group is located. These four regions are self-complementary when the molecules adopt a head to tail and side by side disposition, indicating clearly that this kind of dimeric geometry would be energetically favored.

These structural and electronic characteristics permit the assumption that the radicals will dimerize in a side by side and head to tail fashion through two strong hydrogen bonds. These dimeric entities are actually found in the crystal structure, as shown in Figure 2, and form the secondary structure of this compound. The two molecules that form a dimer are symmetry related through an inversion center and linked together through two identical hydrogen bonds with the following geometric parameters: $d_{O \cdot O}$, 2.696(2) Å; O-H···O, 173°. The packing of dimers in the crystal structure is clearly governed by weak hydrogen bonds of the N-O···H-C type giving rise to the tertiary structure of this compound. This tertiary structure consists of
a herringbone arrangement of dimers forming along the \( bc \) plane molecular sheets that have a "thickness" of two radicals. These dimeric sheets are only linked to each other through weaker interactions, like van der Waals forces, and stack along the crystallographic \( a \) direction forming the quaternary structure. In short, the strong hydrogen bonds assemble the molecules as discrete, zero dimensional, entities (dimers) while weaker hydrogen-bonds control the assembly in two dimensions of the solid.

The crystal structure of radical 3 is also strongly governed by similar strong hydrogen bonds established by the OH group located in the \( para \) position of the aromatic ring. The almost orthogonal arrangement between the N-O axis and the C-O bond that links the OH group to the aromatic ring reduces the possibility of forming a dimeric assembly in a side to side and head to tail fashion similar to that found in compound 2. This has been confirmed by the lack of self-complementary of the electrostatic potential map of the radical. The formation of bonds of N-O···H-O type should of course be expected for radical 3, but in this case they will lead to a different relative arrangement of neighboring molecules. These assumptions are confirmed in the crystal structure of compound 3 in which the assembly of the radicals through N-O···H-O bonds occurs in an angular fashion (\( i.e. \) the long axis of two linked radicals are almost perpendicular) and are in agreement with the computed electrostatic potential map. The asymmetric unit in this crystal structure is formed by two slightly different molecules but the hydrogen bonds always link identical molecules together. The geometry of the intermolecular interactions are defined by the following geometrical parameters: \( d_{\text{O-H}} \cdot \cdot \cdot \text{O} \) \( 2.674(4) \) Å; \( \text{O-H} \cdot \cdot \cdot \text{O} \), \( 165^\circ \) and \( d_{\text{O-H}} \cdot \cdot \cdot \text{O} \) \( 2.690(4) \) Å; \( \text{O-H} \cdot \cdot \cdot \text{O} \), \( 177^\circ \) which are very similar one to each other and agree, as all those found in this series of radicals, with the reported parameters for the usual average hydrogen bonds [16]. The hydrogen bonded radicals form zig-zag chains along the \( a \) axis giving the secondary structure, as depicted in Figure 3. The chains are held together through weak hydrogen bonds that are formed between the free NO group, that is not used in the strong N-O···H-O bond, and two methyl groups of a neighboring molecule. In this way the tertiary structure is formed which consists in flat sheets of molecules that lie in the \( ab \) plane. These molecular planes are stacked along the \( c \) axis and are formed alternately by the two molecules of the asymmetric unit. The packing of such molecular sheets forms the quaternary structure where no significant short contacts can be observed. Roughly speaking, we can say

Fig. 3. — Secondary structures, as found in the X-ray crystal analysis, of (a) radical 3 and (b) radical 5.
that in radical 3 the molecules form strongly hydrogen bonded aggregates, extending in one dimension, with weak hydrogen bonds that link them together in another dimension forming planes. The electrostatic potential map computed for compound 3 has been also shown to be very compatible with the relative 2-D layout of hydrogen bonded molecules observed in the solid state.

After the structural analysis of the above two monohydroxylated radicals we face other cases, such as the radicals 4 and 5, where the structural dimensionalities of the crystalline motifs forming the secondary structures are increased by the placement of two OH groups. Thus, in radical 4 this is achieved by the placement of two OH groups in the meta positions of the aromatic ring. This primary structure permits the propagation of strong hydrogen bonds on both sides of the molecule leading to 1-D crystal motifs. In compound 5, the two OH groups are placed in the meta and para positions permitting the formation of 2-D motifs linked by strong hydrogen bonds.

Radical 4 differs from 2 only by the additional OH group on the second meta position of the aromatic ring. In consequence, the secondary structure of 4 in the solid state can be easily predicted with the previous knowledge of the structure of compound 2. The basic idea is to extend the hydrogen bonded units from dimeric clusters to a 1-D linear chain. In fact the analysis of the crystal structure shows clearly the presence of molecular linear ribbons where each pair of neighboring molecules are linked through two very similar hydrogen bonds, giving rise to the secondary structure depicted in Figure 3. The geometric parameters of these two bonds are: \( d_{O...O} = 2.729(3) \) Å; \( O-H \cdot -O \), 173° and \( d_{O...O} = 2.784(3) \) Å; \( O-H \cdot -O \), 170° which are also quite close to those observed in radical 2. Further analysis of the structure shows the linkage of the molecular ribbons through weak hydrogen bonds of the C-O-H-C type forming the tertiary structure of the crystal which consists of a single corrugated plane of radicals perpendicular to the crystallographic [101] direction. Compound 4 is the second example in this series of compounds where the crystal packing is clearly controlled in one dimension through predictable strong hydrogen bonds while a second dimension of the molecular packing is governed by weak hydrogen bonds.

In radical 5 the aromatic ring has two OH groups, one in a meta position, as in compound 2, and the other one in the para position, as in radical 3. The crystal structure of 5 was solved from its powder diffraction pattern using a rigid body refinement method, since no suitable single crystals could be grown due to its low stability in solution [27]. We can observe that the crystalline motifs previously described for the monosubstituted radicals 2 and 3 are also present in the crystal structure of 5. Indeed, side by side and head to tail arranged dimers, linked through the OH group in meta position (O-H-O distance 2.6(1) Å), are clearly observed. Meanwhile the OH group at the para positions link the resulting dimers together in a angular disposition (O-H-O distance 2.7(1) Å) with the long axis of the linked radical dimers being almost orthogonal. These two different types of hydrogen bonds join the molecules forming the secondary structure of this radical which can be described as a double corrugated molecular sheets parallel to the crystallographic [001] plane. These corrugated planes are stacked parallel to each other along the c axis through van der Waals interactions. In consequence, this compound exemplifies the achievement of a two dimensional control of the disposition of radical units in the crystal packing through the formation of strong hydrogen bonds.

The analysis of the electrostatic potential maps of compounds 4 and 5 reveals quite similar electrostatic features to those found for radicals 2 and 3. Thus, we observe a self-complementary in both maps for a head to tail and side by side disposition, which are very similar to that of compound 2. On the other hand, the electrostatic features around the para OH group in radical 5 are very similar to those of radical 3 and consequently this group is expected to act in a very similar way. In summary, a mere combination of the effects observed in the previous two
monosubstituted radicals can explain quite straightforwardly the formation of the secondary structures of the two disubstituted compounds.

The crystal packing of the two last members of this family of nitronyl nitroxides, radicals 6 and 7, differ very much from those previously described. Interestingly, both radicals show the phenomenon called polymorphism, which consists in the appearance of more than one crystallographic phase. Up to now, two different phases, namely the α- and β-phases [7b,28], are known for compound 6. For the case of radical 7, a second phase has also been observed, but unfortunately its structure is not presently available [9a]. In all reported phases the molecules have an interesting common characteristic such as the presence of a strong intramolecular hydrogen bond. By contrast, their crystal packings are completely distinct. The fact of bearing a OH group in the ortho position of the aromatic ring and the subsequent closeness between this group and the NO group of the same molecule is the reason for the formation of such strong intramolecular hydrogen bonds, which are depicted in Figure 4 for α-phases of radicals 6 and 7. The geometrical characteristics of such intramolecular hydrogen bonds are the following: Radical 6 (α-phase), $d_{O\cdot\cdot\cdotO} = 2.567(3)$ Å, O-H···O 166°; radical 6 (β-phase), $d_{O\cdot\cdot\cdotO} = 2.556(3)$ Å, O-H···O 167°; and radical 7 (α-phase), $d_{O\cdot\cdot\cdotO} = 2.507(2)$ Å, O-H···O 161°. These geometrical data are very close one to each other while there are significant differences when they are compared with those found for the previous radicals. Thus the O-H···O angles in these crystalline phases are certainly smaller than those found for other radicals in which the hydrogen bonds take place intermolecularly. An effect that can be ascribed to the rigid intramolecular geometric constraints imposed by the primary structures of both radicals.

In any of the two phases of radical 6, three-centered strong hydrogen bonds have been observed. Such interactions are a particular type of a hydrogen bond in which one hydrogen atom is non covalently bonded to two hydrogen bond acceptor groups (O,N,···) at the same time [16]. In consequence, in both phases of compound 6, the intermolecular arrangement is governed only through weak interactions, such as weak hydrogen bonds of N-O···H-C type or van der Waals forces. Thus, according to the given definition of secondary structures in both phases of radical 6 the secondary structures agree with the primary one since they are formed by only one single molecule. This fact makes that in the α-phase of 6 a network of weak hydrogen bonds is present in all the three crystallographic directions in which quite short intermolecular distances occur (N-O···H-C distances: 2.60 – 2.87 Å). By contrast, the β-phase of radical 6 shows a pattern with a much lower dimensionality. The molecules are arranged in sheets within the crystallographic bc plane. In these planes the molecules form weak hydrogen
bonds only in the $b$ direction, while no short contacts can be appreciated along the $c$ axis. Summarizing, the $\alpha$-phase of 6 shows a quite isotropic arrangement of radicals where the weak hydrogen bonds, that induce the shortest intermolecular contacts, exist in all three spatial directions, while in the $\beta$-phase the weak hydrogen bonds are only observed in one direction being such arrangements their tertiary structures.

The $\alpha$-phase of radical 7 is the unique example in this series of compounds in which the crystal structure shows a strong intermolecular hydrogen bond set up between two OH groups. This interaction is defined by the parameters: $d_{O-O} = 2.751(2)$ Å and O-H $\cdots$ O, 170° and is responsible for the formation of 1D hydrogen bonded arrays along the crystallographic $c$ direction. Furthermore, two neighboring arrays are additionally linked through three center hydrogen-bonds, with geometrical parameters $d_{O\cdots O} = 2.999(2)$Å and O-H $\cdots$ O, 101°, established between the already intramolecularly linked NO groups and the ortho OH groups of radicals related by inversion centers. This bifurcated hydrogen bond generates an extraordinarily short NO $\cdots$ ON contact of 3.159(2)Å between the involved radicals. In addition, several weak hydrogen bonds are found among the non-intramolecularly bonded NO groups and methyl groups along $b$ direction and aromatic hydrogen atoms along $a$ direction. These weaker interactions join the double bonded chains together in the two remaining directions. According to the given definition of secondary and tertiary structures, in this crystal the secondary structure is a double chain of radicals while the whole crystal should be regarded as the tertiary one.

5.1.2. General Structural Considerations. — The polymorphism observed in radicals 6 and 7 introduces an additional characteristic of some molecular solids that reflects a supplementary difficulty in the prediction of their crystal structures. Some remarks are to be made on this point. It should be stressed out that no intermolecular strong hydrogen bonds are established in any phase of radical 6 neither in the $\alpha$-phase of 7. Moreover, in all these crystalline phases the forces linking together the molecules are always very weak. Two other examples of $\alpha$-nitronyl nitroxides presenting polymorphism have been reported so far. Such examples are the $p$-nitrophenyl $\alpha$-nitronyl nitroxide radical (8) [29] and the most simple member of this family of radicals, the $\alpha$-nitronyl nitroxide radical 9 [30]. In both cases the intermolecular forces responsible for their crystal packings are weak hydrogen bonds having important consequences on their magnetic properties.

![Image](image.png)

In radical 8 up to four different stable phases are known, while for radical 9 only two phases, stable at room temperature, have been reported. A qualitative conclusion can be extracted from the above mentioned observations. If strong forces link the molecules together, the degrees of freedom that the resulting molecular entities (clusters, dimers, chains or planes) may have
in order to build up the crystal packing seem to be reduced and, consequently, less polymorphs are observed. In other words, when only weak forces control the packing of molecules, several similar energetic wells can be found in the multidimensional space. Thus, depending on the experimental conditions (solvent and temperature) several polymorphs can be obtained.

Another important point to be stressed out is the structural role played by hydrogen bonds in the supramolecular organizations of α-nitronyl nitrooxide radicals. Thus, most of the crystal structures described in this review have been shown to be governed by highly directional strong hydrogen bonds. This type of interactions have very similar geometric parameters (O⋯O distances and O-H⋯O angles) and, consequently, they govern in a high degree the relative arrangement of molecules of the supramolecular organizations. A carefully analysis of all the above described crystal structures reveals that the relative location of OH groups around the ONCNO groups of neighboring molecules is clearly clustered in three groups depending almost exclusively on the topology of the OH groups of the aromatic ring. As depicted schematically in Figure 5, radicals with a OH group in the para position appear grouped in region (a), while radicals with OH groups at the meta position are all grouped in region (b). The third assembly, noted as (c), corresponds to radicals with ortho OH groups. As can be easily observed, the strong hydrogen bonds in this kind of compounds are highly directional and force the relative arrangement of molecules into well-defined conformations that must correspond to distinct energy wells. A second consequence of this analysis is the observation that there is a clear preference for the hydrogen atoms to be located around the non-bonding orbitals of the oxygen atom of the NO groups: as it has also observed for many other classical hydrogen bonds [31]. Exceptions to this rule are the cases in which the OH groups are at the ortho position where intramolecular steric hindrances force the hydrogen atoms to lie in a quite different position.

Furthermore, it can be seen from the previous analysis of the described structures, that different dimensionalities are achieved both in the secondary and in the tertiary structures of radicals 2 to 7. In addition, the secondary structures of these radicals are fairly well rationalized, while the tertiary ones are much more unpredictable. The described structural analysis does not pretend to answer completely the complex questions concerning the prediction of crystal structures but merely emphasizes that a deep knowledge of the behavior of hydrogen bonds in a given family of compounds makes it possible to perform some predictions about the structural features and motifs for a new member of this family. In the context of a search for a systematic way of designing molecular magnetic materials, the present results show that, up to a certain degree, the crystal structures can be described in terms of the dimensionalities described above and hence they are predictable in some aspects. Moreover, theoretical tools
such as the computation of the electrostatic potential maps can increase the degree of certainty for the prediction of a specific molecular arrangement in a crystal structure.

Finally, it should be pointed out that in all the described examples, only in radical 7 one finds O-H - O contacts between two OH groups. Hydrogen bonds almost always take place between the OH groups and one of the NO groups. This result points towards an energetic preference of the OH groups to form hydrogen bonds with NO groups instead than with oxygen atoms of other OH groups, that are also potential hydrogen bond acceptors. The latter type of hydrogen bonds will only be favored in cases where the structural conditions favor them: as for example when the ratio between the number of OH and NO groups is increased. To our knowledge, these kind of bonds has only been observed in the α-phase of radical 7, described by Sugawara et al. [9a].

Up to now we have seen the usefulness of hydrogen bonds to control, up to a certain extension, the molecular arrangement of radicals in the solid state. As a second step, a correlation between the different molecular layouts and their magnetic properties should be worked out. If this second goal is achieved, an important step ahead towards the design of tailor-made magnetic materials using hydrogen bonds would have been made.

5.2. Magnetic Properties of Hydroxylated Radicals. — The magnetic properties of organic/molecular solids are usually interpreted by the magnetic mechanisms already described in the previous Sections. In consequence, two different kinds of close contacts or intermolecular interactions in molecular solids made up of α-nitronyl nitroxide radicals must be searched for very carefully. One of them are the close contacts between two main spin carrying units — the ONCNO moieties — of neighboring molecules. The other ones are the close contacts between one of these main spin carrying units and other groups of a neighboring molecule bearing only a small spin density on it. The last groups may be the hydrogen atoms of either OH, CH₃, or ArH groups: since they use to carry small spin densities and tend to establish hydrogen bonds, either strong or weak, with N-O groups. Consequently, only those close contacts involving at least one group with large spin density are likely to be of magnetic interest. By contrast, those others involving only groups with very small spin densities seem have no magnetic significance.

It should be also stress that the nature of the magnetic coupling due to the two aforementioned types of close contacts is strongly dependent on the relative geometry of the interacting groups. Thus, if there is a large orbital overlap integral among the interacting sites, the normal magnetic coupling inferred from the signs of the spin densities are expected. On the contrary, if the overlap is large but the overlap integral is almost zero (orthogonality), the strength will diminished and the nature of the coupling can be even reversed [1c]. For such reasons, special care has to be taken in the establishment of magneto-structural correlations extracted only from X-ray and static magnetic susceptibility data. In some cases, in order to extract more precise information about the magnetic pathways present in a crystalline solid, additional experiments should be done on single crystals or even on crystalline powders. The rotation of single crystals with respect the static magnetic field in a EPR spectrometer [32], and ac-susceptibility, heat capacity measurements, or muon spin rotation experiments [33], performed either with single crystals or powder samples, can give valuable information about the dimensionality and paths of the magnetic interactions.

In the present family of compounds some of the already described magneto-structural correlations have been done using static susceptibility measurements and crystal structures. As will be shown later, the obtained correlations demonstrate that in addition to a certain structural control achieved through the hydrogen bonds, a certain control of the magnetic properties can also be obtained.
5.2.1. Detailed Macroscopic Magnetic Properties. — The temperature dependence of the magnetic susceptibility of radical 2 can be described by the Curie-Weiss law, \( \chi = C/(T - \theta) \), with a Curie constant of 0.374 emuKmol\(^{-1}\) and a Weiss constant of \(-2.80(3)\) K. Accordingly, the effective magnetic moment decreases continuously upon cooling, as shown in Figure 6, indicating the presence of weak intermolecular antiferromagnetic interactions among the \( S = 1/2 \) species. This result, together with the information obtained from the crystal structure, can be analyzed as follows. Looking at the best fit of the susceptibility measurements, the magnetic interaction in the solid can be supposed to take place in several spatial directions. If the hydrogen bonded dimers were found to be the unique path for the intermolecular magnetic exchange interactions, the static magnetic susceptibility data should fit to a Bleaney-Bowers model \([34]\), and not to the Curie-Weiss law. In other words, the unpaired electron of each radical molecule interacts magnetically with more than one neighboring molecule. Three structural aspects could explain the macroscopic magnetic behavior. First, within a dimer the shortest intermolecular atomic distances are those involved in the strong hydrogen bond. As a consequence of the proximity of the two molecules, a short intermolecular distance of 4.05 Å between the two NO groups is found being this close contact relevant for the magnetic interactions. Thus, we can strongly suspect that the observed dimeric geometry — the side by side and head to tail disposition — produces an antiferromagnetic coupling between the unpaired electrons. Second, among the dimers a complex network of weak hydrogen bonds is present. Through these bonds several quite short intermolecular distances are observed within the \( bc \) plane. The third structural characteristic that should be pointed out is the existence of a short NO · · · ON intermolecular distance of 3.92 Å between two molecules belonging to two different dimers and that is established along the crystallographic \( a \) axis. Therefore, these three structural features could nicely explain the high dimensionality of the observed macroscopic static susceptibility but they cannot give any clear clue about the actual magnetic paths in the solid. EPR studies on an oriented single crystal of radical 2 have shown that the hydrogen bonded dimers are not magnetically isolated in accordance with the susceptibility measurements \([32a]\).
As shown in Figure 6, static susceptibility measurements of radical 3 show a completely opposite magnetic behavior to that previously described. Thus, a continuous increase of the effective magnetic moment with decreasing temperature is observed which is a signature of the presence of dominant ferromagnetic intermolecular interactions. A precise fit of the experimental data is only achieved by using low dimensional models with dominant ferromagnetic interactions. For example, a 2D square lattice magnetic model [35] with an intraplane ferromagnetic exchange interaction. $J_{\text{intraplane}}/k_B = +0.63$ K, taking into account an interplane interaction [36], $J_{\text{interplane}} = -0.56$ K, assuming a number of nearest neighboring planes of 2, reproduces completely the experimental susceptibility data over all the studied temperature range.

Owing to the small magnitude of the involved exchange coupling constants, the exact magnetic dimensionality can not be extracted conclusively only form these data. For this reason additional EPR experiments on oriented single crystals of 3 [32] and, additionally, zero and transverse field muon spin rotation experiments on a powder sample [37] were carried out. Both experiments confirmed the 2D ferromagnetic character of this compound and also showed that the magnetic planes coincide with the crystallographic planes where the hydrogen bonded molecules are located. Therefore, there must be some correlation between the observed ferromagnetic interactions and the layered crystalline structure. Indeed, the shortest intermolecular distances occur within the layers while the intermolecular NO⋯ON distances along this plane are rather large (at least 5 Å). Both structural features suggest that the ferromagnetic interactions should be explained through the participation of the 2D network of hydrogen bonds, that provoke a T-shaped relative arrangement of radicals. This fact allows us to assume that this geometrical disposition prevents the appearance of antiferromagnetic interactions and at the same time induces a ferromagnetic interaction between the involved unpaired electrons.

Up to now we have seen that two different relative geometric dispositions induce opposite magnetic interactions. While the head to tail and side by side disposition of two α-nitronyl nitrooxide radicals, linked through hydrogen bonds, favors the establishment of antiferromagnetic intermolecular interactions, the T-shaped arrangement of hydrogen bonded molecules seems to be responsible for ferromagnetic ones. These two opposite effects, produced by two well defined and different geometrical arrangements of hydrogen bonded radicals in the solid state, were also observed in other cases where both structural patterns appear.

Static magnetic susceptibility data of radical 4 show a continuous decrease of the effective magnetic moment, with lowering temperature as shown in Figure 6. Thus, antiferromagnetic interactions seem to be predominant in this molecular solid. The experimental data are best fitted with the polynomial expression corresponding to a model of isolated chains of antiferromagnetically coupled Heisenberg $S = 1/2$ spins [38]. The value of the exchange interaction is estimated to be $J/k_B = -2.84(5)$ K from this fit. This result can be interpreted in relation to the crystal structure in terms of an extension of the antiferromagnetic interaction observed in the dimers of 2 to both sides of radical 4 in agreement with extension of the structural dimensionality from a 0-D cluster (dimer) to a 1-D chain.

In radical 5 most of the structural features observed for the monohydroxy substituted radicals 2 and 3 are simultaneously kept. Thus, the concurrent presence of the dimeric geometry of compound 2 together with the T-shaped intermolecular conformation of radical 3 leads us to expect a coexistence of both ferro- and antiferromagnetic intermolecular interactions. As shown in Figure 6, an increase of the effective magnetic moment with lowering temperature is observed for radical 5, reaching a maximum of the $\chi T$ product at 7 K, while on further cooling the effective magnetic moment decreases quite rapidly. The best fit to the experimental data requires the use of a model that takes into account three different exchange parameters which is in accordance with the molecular packing. First, a linear Heisenberg chain of $S = 1/2$.
units with alternating exchange interactions explains the antiferromagnetic interaction associated to the dimeric geometry, $J_{\text{intradimer}}$, and the ferromagnetic interaction expected for the T-shaped interdimer arrangement. $J_{\text{intradimer}}$, [39]. Second, an additional small interchain antiferromagnetic interaction, $J_{\text{interchain}}$, is necessary to achieve a complete fit of the experimental data [35]. The resulting values for the coupling constants obtained from this fit are as follows: $J_{\text{intradimer}}/k_B = +9.3$ K, $J_{\text{intradimer}}/k_B = -3.8$ K, and $J_{\text{interchain}}/k_B = -0.34$ K; assuming 4 nearest neighboring chains. A noteworthy point of these results is the similarity of the coupling constants within the dimers of radicals 2 and 5, which is in agreement with similar geometric dispositions.

As depicted in Figure 6, the magnetic behavior of the two phases of radical 6 are completely different in accordance with their different crystal structures. While the dominant intermolecular interactions in the $\alpha$-phase are ferromagnetic and have a high dimensionality, in the $\beta$-phase they are antiferromagnetic and have a low dimensionality. Thus, the static susceptibility data of the $\alpha$-phase can be fitted in the whole temperature range to the Curie-Weiss Law, with a Curie constant of 0.359 emuKmol$^{-1}$ and a positive Weiss constant of $\theta = +0.63$ K, indicating the presence of high dimensional ferromagnetic interactions. From the crystal structure we know that a complex network of weak hydrogen bonds are established in all the crystallographic directions. By other hand, the intermolecular NO···ON distances have shown to be similar in all directions but these NO groups are nearly orthogonal to one other. These structural characteristics seem to favor the establishment of ferromagnetic interactions in the $\alpha$-phase of 6 that give rise to the bulk ferromagnetic ordering observed at 0.45 K [7b].

By contrast to this bulk ferromagnetism, the static magnetic susceptibility measurements of the $\beta$-phase show a decrease of the effective magnetic moment upon cooling, as shown in Figure 6 [40]. The best fit of the data corresponds to a 1D antiferromagnetic chain with antiferromagnetic interactions, $J_{\text{intradimer}}$, taking into account weak ferromagnetic interactions between these chains. $J_{\text{interchain}}$. The parameters obtained with this model are $J_{\text{intradimer}}/k_B = -1.31$ K and $J_{\text{interchain}}/k_B = +0.7$ K; assuming 4 nearest neighbors. Such a magnetic behavior can be rationalized as follows. The only short intermolecular interactions occur along the crystallographic $b$ axis, while along the $c$ axis no magnetically relevant contacts can be observed. On the other hand, the shortest contact between NO moieties in $b$ direction takes place among two almost coplanar ONCNO groups with O···O intermolecular distances of 3.82 Å. These two facts might explain both the low dimensional magnetic behavior of this phase and the negative sign of the magnetic exchange interactions.

The magnetic susceptibility of a polycrystalline sample of the $\alpha$-phase of radical 7 revealed the presence of high dimensional ferromagnetic interactions. The experimental values follow the Curie-Weiss law with a Curie constant of 0.383 emuKmol$^{-1}$ and Weiss constant of $+0.8$ K [9a]. This result is in accordance with the multiple intermolecular contacts found in the crystal structure which could be responsible for its almost isotropic bulk magnetic behavior. Indeed, the $\alpha$-phase of radical compound 7 shows a ferromagnetic phase transition at 0.5 K.

5.2.2. General Magneto-Structural Correlations. — As a conclusion of the analyses of the magnetic properties of this family of compounds some general comments and problems should be pointed out. First of all, it should be stressed that the analysis of the magnetic pathways in molecular solids composed of organic open-shell repeating units is not a straightforward task. We have seen that two crucial points must be carefully analyzed in order to explain the macroscopic magnetic behaviors. First, the intermolecular contacts between the main spin carrying units — the ONCNO moieties — and their geometric layouts should be carefully analyzed. Second, the shortest intermolecular contacts between one of such a ONCNO group of one molecule and groups of neighboring molecules carrying small amounts of spin should also
be taken into account. In this second point, special attention should be paid to the hydrogen
bonds, either weak or strong, and their layouts with respect the ONCNO moieties. In some
cases, these structural analyses yield a quite clear description of the magnetic pathways and
properties. However, in others, these analyses do not provide enough clear insights on the
magnetic pathways since different dimensionalities, or even different signs of the exchange
interactions, can be found depending on the relative importance given to one or another type
of close contacts.

A more rigorous systematization of all the intermolecular close contacts should be performed
in the near future in order to understand clearly what is really going on in this kind of materials.
The examples given in this work, in which radicals are forced to be arranged in definite ways,
may be used as a step ahead in order to increase the knowledge about the transmission of
magnetic interactions in organic solids.

6. Conclusions and Perspectives

As explained throughout this review, one of the most exciting subjects in molecular magnetism
is the establishment of clear magneto-structural relationships in purely organic materials. In or-
der to achieve this goal, supramolecular design elements should be developed to provide strong
enough intermolecular forces with high directionality in order to control the relative mole-
cular arrangements. Up to now, in the family of α-nitronyl nitroxide radicals only coulombic
interactions and hydrogen bonds have been used with such a purpose.

For the advance of knowledge about the magnetic interactions in molecular solids or even for
a prediction of magnetic properties, the crystal packing modes of these solids should not be left
to chance. In this sense, the work in the near future should be devoted to the preparation of
molecular solids with increasing predictability of crystal packing. The use of hydrogen bonds
as a main driving force for joining heteromolecular building blocks, as recently proposed by
Akita et al. [41] is a subject worth studying. Furthermore, the use of hydrogen bonds in
magnetic molecular materials should be extended to other molecular solids, built up by radical
molecules other than the α-nitronyl nitroxide radicals. Moreover, the possibility of making
mixed crystals mixing in certain proportions two or more different building blocks seems to be
very appealing. The resulting blends or alloys can be extremely interesting to be studied both
structurally and magnetically.

The positive results obtained for the preparation of molecular magnetic solids with hydrogen
bonds as supramolecular design elements opens the possibility of using them in the formation
of high-spin supramolecular aggregates in solution. These supramolecular entities could have
a controllable dimensionality and nanoscopic sizes being extraordinarily interesting in two
senses. First, they may enable the study of the magnetic properties of discrete polymolecular
units of open-shell compounds, permitting the extraction of essential information in order to
understand the magnetic properties in the solid state. Second, their behaviors in solution may
themselves be very interesting, exhibiting new and even previously unknown magnetic and/or
optic properties.

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References


[22] See Ref. [16], Chapter 2, p. 29.
[40] Veciana J. et al., unpublished results.