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Molecular ferromagnets

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Abstract. The state-of-the-art, achievements, problems and prospects of an actively developing area of supramolecular chemistry, *viz*., the design of molecular ferromagnets, are considered. The bibliography includes 343 references.

I. Introduction

This review deals with a rapidly developing area of modern chemistry, *viz*., the design of molecular ferromagnets. Like any other area of natural sciences which is still in its infancy, it is not yet liable to generalisations, as many works are pioneering. Various approaches are used to solve the diverse problems arising in these studies, which require a high level of integration of the efforts of specialists in different fields of knowledge. Nevertheless, certain approaches to the design of molecular ferromagnets have now taken shape.[1–18]

It is obviously impossible for a single review to consider every aspect of the design of molecular ferromagnets in detail. Therefore, in this paper we dwell on the basic classes of the chemical compounds which are characterised by established synthetic strategies and the principal ways for the construction of highly dimensional multispin systems.

When the development of methods for the synthesis of highly dimensional systems is concerned, one has, to some extent, to part with the classical chemical thinking, which generally deals with the design, modification or transformation of an individual molecule. No doubt, a molecule taken as a subunit is also important. However, the arrangement of the molecules is no less important in the design of molecular ferromagnets. Even more important is their selective arrangement in a highly dimensional assembly. Arrangement of individual molecules in a highly effective assembly bound by exchange interactions is a key problem in the design of molecular ferromagnets. Before we start a detailed discussion of this problem it is necessary to define the notion of a 'molecular ferromagnet'.

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The term 'molecular ferromagnet' may seem to a certain degree paradoxical. The classical ferromagnet is a macroobject, for example, a piece of iron, nickel, or cobalt or an alloy of these metals, but in no way a separate molecule. By its very nature, a magnetic phase transition into the ferromagnetic state is a cooperative phenomenon inherent in a macroobject as a phase. Nevertheless, in recent years the term 'molecular ferromagnet' has been widely used in scientific publications dealing with the design of multispin systems.† Let us define the essence of this term more precisely.

The studies in the field of molecular ferromagnets deal with the synthesis of organic, organometallic and, currently, mostly coordination compounds the solid phases of which are formed from separate molecules or ions that existed initially in a solution and contained paramagnetic centres. In these solid phases, as in classical ferro- and ferrimagnets or weak ferromagnets, magnetic phase transition into the ferro-, ferrimagnetic or weak ferromagnetic state is detected below a critical temperature.

These days, researchers can plan beforehand, with a certain degree of success, the synthesis of compounds with a desired solid state structure that will be formed from molecular precursors in solution. These molecules should form layered or framework polymers when crystallised from solution. As a matter of fact, this field of studies which implies the design of highly dimensional structures is the subject of supramolecular chemistry.

The formation of layered or framework structures in the solid phase of molecular ferromagnets is a prerequisite for the magnetic phase transition into the ferromagnetic state. This condition is necessary but insufficient in the chemical design of molecular ferromagnets. For this transition to occur, the paramagnetic centres in polymers should be linked with such an atomic chain serving as an exchange channel[13] that the polymer has the ability to undergo magnetisation in a magnetic field. The following consideration is important in this case: the higher the efficiency of the exchange channels in exchange interactions between the unpaired electrons of the paramagnetic centres the higher critical temperature (T_c) that can be achieved. It is within the limits set by these requirements that regular studies of the effect of conditions of directed chemical synthesis on the magnetic parameters (the

† Reviews and monographs on 'molecular ferromagnets' have been published, the titles of which, like the present paper, sometimes contain this word combination (or the equivalent expressions: 'molecular magnetics', 'molecular magnets', 'molecule-based ferromagnets') as the key words.[1–14]

Curie temperature or the Neel temperature, spontaneous magnetisation, *etc*.) of the final magnetically active product are being performed, *i.e*., the effects of the composition, structure of the starting molecules, conditions of the synthesis and crystallisation on the magnetic properties of the resulting solid phases are being studied. Magnetic-structural relationships understood as relationships between the observed magnetic properties of a compound and its chemical and structural characteristics are used in the search for subjects with the required properties. These relationships are either calculated or determined experimentally.

Thus, the word 'ferromagnet' in the term 'molecular ferromagnet' is used in the ordinary sense, while the definition 'molecular' reflects the methodology of the approach: the starting individual molecules and/or molecular ions should have a structure which would enable them to form a spatial structure favourable for a magnetic phase transition during formation of a solid phase. The problem can be solved by various chemical methods combined by the term 'chemical design of molecular ferromagnets'.

The development of principles for the synthesis of molecular ferromagnets and the determination of their inherent magnetic-structural relationships are fundamental problems. There are few natural magnetic materials. Most of them are transition metals and their oxides; the number of magnetic materials was mainly increased by virtue of metal alloys and binary oxides. However, studies on the design of molecular ferromagnets make it possible to expand considerably the range of magnetically active compounds and magnetic materials. In addition, the design of molecular magnets and conventional, mild synthetic approaches provide a possibility to create new magnetic materials using technologies alternative to the traditional power-consuming metallurgical technologies for the production of magnetically active oxide materials.

The number of studies in the field of the design of molecular ferromagnets increases rapidly. Owing to the aforementioned high integration requirements concerned with the problem, experts in the field of inorganic, organometallic or organic chemistry and in materials science, chemical physics and physics of magnetism are involved in collaboration. The results of these studies are extremely 'scattered' in scientific publications; therefore, biennial international conferences on molecule-based magnets play an important uniting role (see, *e.g*., Refs 15 and 16). The proceedings of these conferences are published in the journal *Molecular Crystals and Liquid Crystals* (see, *e.g*., Refs 17 and 18). However, these are far from being the only international conferences with scientific sections devoted to molecular ferromagnets (see, *e.g*., Refs 19 and 20).

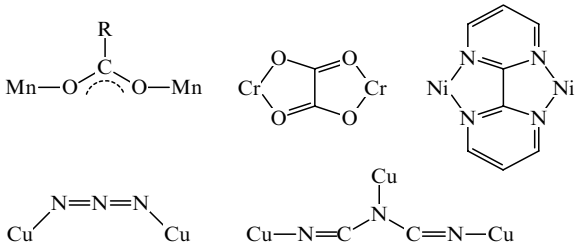
In this review, we made an attempt at the generalisation and systematisation of the main approaches and strategies existing at present in the field of the synthesis of molecular ferromagnets. As a rule, the design of particular compounds triggers an entire complex of studies dealing with the analysis of structure, magnetic-structural relationships and mechanisms of exchange interactions between the unpaired electrons in paramagnetic centres. In all of the molecular ferromagnets discussed in the present review the structure of a molecule or a bridging ligand involves at least one carbon atom. The presence of one carbon atom, or better several carbon atoms, reflects the common desire of the researchers to use as soon as possible all the potential of synthetic organic chemistry in the given area.

Here we do not consider the classical magnetically active systems in which the metal atoms in the solid phase are separated by the individual oxygen, carbon, sulfur, halogen or boron atoms.

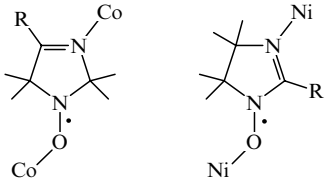
II. Systematisation principles

For a systematic generalisation of chemical compounds involved in the design of molecular ferromagnets, we offer a specific 'language'. It is therefore reasonable to discuss the principles underlying its construction. In this work we speak of metal-containing molecular ferromagnets as being two or three-dimensional systems (as regards their structures);‡ hence the common features of all of the systems under consideration are the presence of a paramagnetic metal ion in a compound and the presence of a bridging group of atoms linking the metal ions to form a layer or a framework. Therefore, the description of a particular system can be given by the key formula MnM′, where M and M′ are paramagnetic metal ions (the same, different or existing in different oxidation states) and n is the smallest number of atoms in a bridging unit connecting the M and M′ ions.

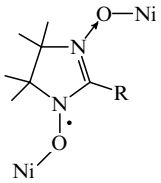
Thus, we shall refer cyanide complexes of metals containing, *e.g*., such fragments as $V^{3+}-C\equiv N-V^{3+}$, $Cr^{3+}-C\equiv N-Ni^{2+}$ and $Fe^{2+}-C\equiv N-Fe^{3+}$ to the M2M′ class, since the bridging cyanide is a diatomic unit. Carboxylate, oxalate, bipyrimidine, azide or dicyanamide polynuclear complexes containing triatomic bridges as the shortest ones belong to the M3M′ class.



According to the above approach, the complexes with 3- and 2-imidazoline derivatives are regarded as M4M′ systems.

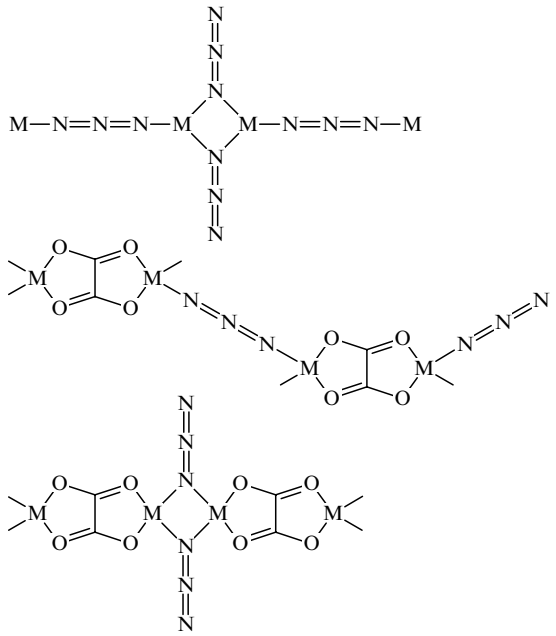


Heterospin polynuclear metal complexes with nitronyl nitroxyl radicals or 2-imidazoline 3-oxide paramagnetic derivatives, which play the bridging role, belong to the M5M′ systems.



More complicated situations are also possible where one bridging ligand can form exchange channels with different numbers of atoms between the metal ions or the bridging function is played by several ligands creating the exchange channels with different numbers of bridging atoms. We designate such systems as Mnn'M′, if the ligands are the same, and Mn(n')M′ if the ligands are different. Fragments of an M31M′ system with one ligand and M3(3)M′ and M3(1)M′ systems with different bridging ligands are shown below as examples.

‡ It should be noted that structural dimensionality, *i.e*., molecular (zero-dimensional), chain (one-dimensional), layered (two-dimensional) and framework (three-dimensional) compounds, should not be confused with magnetic dimensionality, *i.e*., isolated exchange clusters (zero-dimensional), exchange chains (one-dimensional), *etc*.; in many cases, the structural and magnetic dimensionalities do not correlate.

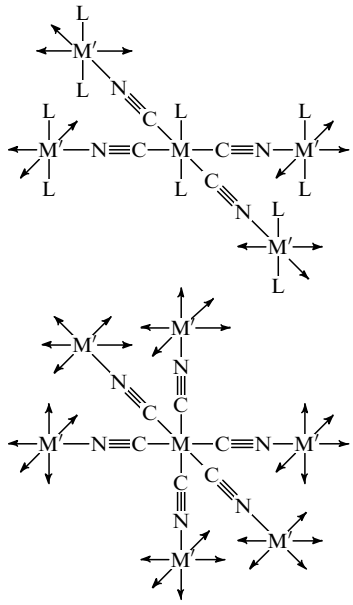


The systematisation suggested here is general and is not limited to specific metal ions or bridging ligands.

III. M2M′ systems

The molecular ferromagnets of the M2M′ class primarily include coordination compounds with the bridging cyanide ligands. The ability of homo- and heterometallic hexacyanides to undergo ferro- and ferrimagnetic ordering at low temperatures has been known for a long time (see, *e.g.*, Refs 21 and 22). However, the problem was recently considered in a different way[23–31] and an essentially new contribution to the design of high-temperature molecular ferromagnets of the M2M′ type based on metal cyanide complexes was made.

The first synthetic coordination compound, *viz.*, Prussian blue, whose framework structure was established by Buser *et al.*,[32] may be considered as an ancestor of this group of molecular ferromagnets. The highly symmetrical octahedral coordination anion $[M(CN)_6]^{n-}$ serves as a starting block for the construction of two- and three-dimensional structures.[33] If an additional M′ ion is introduced, the system can undergo polymerisation along two or three mutually perpendicular directions.



Prussian blue itself, $Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot xH_2O$ ($x = 14-16$), has a framework structure (cubic face-centred structure) and undergoes a magnetic phase transition at 5.6 K.[34] The low temperature of the magnetic ordering is due to the fact that the Fe^{II} ion is in the low-spin d^6 state. As a result, the exchange interactions between the paramagnetic centres (the Fe^{III} ions) located in the $Fe^{III}-N\equiv C-Fe^{II}-C\equiv N-Fe^{III}$ fragments at a distance of 10.6 Å from each other are rather weak.[26] Thus, it seemed reasonable to assume that the magnetic ordering temperature will be higher if all of the metal ions are paramagnetic. Verdaguer *et al.*[23–31] were the first to perform a directed synthesis of Prussian blue analogues in which the iron ions were replaced by other metal ions in variable ratios. Table 1 presents some data for hexacyanometallates of the general formula $M_3[M'(CN)_6]_2$ from which it is possible to follow the regularities of changes in the magnetic ordering temperature (we do not specify its type, *i.e.*, ferromagnetic, ferrimagnetic or antiferromagnetic).

Table 1. Magnetic ordering temperatures for hexacyanometallates $M_3[M'(CN)_6]_2$.

M	T_c /K	M	T_c /K
$M_3[Cr(CN)_6]_2$		$M_3[Mn(CN)_6]_2$	
V^{II}	315	Mn^{II}	37
Cr^{II}	240	Ni^{II}	37
Cu^{II}	66		
Mn^{II}	60	$M_3[Fe(CN)_6]_2$	
Ni^{II}	53	Cu^{II}	20
Co^{II}	23	Mn^{II}	9
Fe^{II}	16	Ni^{II}	23
		Co^{II}	15

In a series of complexes containing the $[Cr(CN)_6]^{3-}$ anions, the values of T_c are always higher than those for the analogues with the $[Mn(CN)_6]^{3-}$ or $[Fe(CN)_6]^{3-}$ anions; the highest T_c values are observed for $V_3[Cr(CN)_6]_2$ and $Cr_3[Cr(CN)_6]_2$. The latter is commonly depicted as $Cr_5(CN)_{12}$. Thus, there is an obvious trend of the increase in the critical temperature if the compounds involve V^{II}, Cr^{II} and Cr^{III} containing a significant number of unpaired electrons in the t_{2g} orbitals. Hexacyanometallates $(Et_4N)_{0.5}Mn_{1.25}[V(CN)_5](H_2O)_2$ (T_c = 230 K), $Cs_2Mn[V(CN)_6]$ (T_c = 125 K),[30] $Cs_{0.75}[Cr_{2.125}(CN)_6]$ (T_c = 190 K)[25] characterised by high T_c also contain the V^{II} or Cr^{II} ions, which is not quite convenient from the practical viewpoint as they are unstable in this oxidation state under ordinary conditions. Nevertheless, the compound $V^{II}_{0.42}V^{III}_{0.58}[Cr^{III}(CN)_6]_{0.86} \cdot \cdot 2.8H_2O$ with T_c = 315 K obtained in an inert atmosphere (it is sensitive to the atmospheric oxygen) retains its magnetic properties for several weeks when dispersed in kerosene or mixed with a glue.[27] Based on this compound, a thermomagnetic switch and a device for the absorption of solar energy were designed and these were shown to function properly.[24,35]

The character of exchange interactions in the $M-N\equiv C-M'$ clusters can be predicted with high reliability under the assumption that these interactions between the unpaired electrons on the e_g orbitals of one metal and the unpaired electrons on the t_{2g} orbitals, orthogonal to the former, of another metal should be ferromagnetic, while the interactions between the unpaired electrons on the t_{2g} orbitals of both metals should be antiferromagnetic.[23–25,36,37] By calculating the number of possible channels of exchange interaction according to the ferromagnetic (F) and antiferromagnetic (AF) mechanisms, it is possible to predict the character of ordering in the solid phase of a specific hexacyanometallate. Below the critical temperature, ferromagnetic ordering

of the spins of the paramagnetic centres predominates if F > AF, and antiferromagnetic ordering predominates if AF > F.

According to this scheme, in all of the hexacyanometallates with $T_c > 100$ K discussed above, where the $t_{2g}-t_{2g}$ interactions predominate and the exchange interactions between the paramagnetic centres of the neighbouring metal ions are antiferromagnetic, the magnetic moments of the sublattices of one metal ion are partially compensated by the magnetic moments of the sublattices of the other metal ion below the critical temperature. In systems of the type $Ni_3[Cr(CN)_6]_2$ and $Cu_3[Cr(CN)_6]_2$, the unpaired electrons lie on orbitals of different symmetries (e_g and t_{2g}), and the exchange interactions between the paramagnetic centres in these systems are ferromagnetic, which is favourable for the synthesis of compounds with high spontaneous magnetisation.[23]

The results obtained [23–31] stimulated the study [38, 39] of a series of solids $(Ni^{II}_xMn^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]\cdot 8H_2O$. The solids with this composition were obtained in two ways:

(1) by mechanically mixing pure $Ni_{1.5}[Cr(CN)_6]\cdot 8H_2O$ and $Mn_{1.5}[Cr(CN)_6]\cdot 7.5H_2O$; in the former, the unpaired electrons of the neighbouring paramagnetic centres (Ni^{II}, Cr^{III}) are coupled by ferromagnetic exchange interactions [the exchange interaction integral (J) is positive]; in the latter, the spins of the neighbouring centres (Mn^{II}, Cr^{III}) mostly interact antiferromagnetically ($J < 0$);

(2) by mixing at the molecular level, *i.e.*, in the synthesis of $(Ni^{II}_xMn^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]\cdot 8H_2O$; the value of x was set by the initial ratio of the reagents $NiCl_2$, $MnCl_2$ and $K_3Cr(CN)_6$.

As expected, the characteristics of the mixture obtained by the former method are additive values proportional to the fractions x and $1-x$ of the mixed compounds; for example, the magnetisation of the mechanical mixture grows linearly as x increases from 0 to 1. The variation of the characteristics of the phase obtained by the latter method (magnetisation, the Weiss temperature, coercive field) with x is essentially different due to the competition between the ferro- ($J > 0$) and antiferromagnetic ($J < 0$) interactions. As a result, *e.g.*, the spontaneous saturation magnetisation (J_s) quickly decreases from 4.38 μ_B to almost zero when x increases from 0 to 0.43; when x increases from 0.43 to 1, J_s quickly increases from ~ 0 to 5.57 μ_B according to the equation

$$J_s = 2\mu_B\left|\frac{3}{2}+\frac{3[x-2.5(1-x)]}{2}\right|.$$

The coercive field is a maximum (680 G) at $x \simeq 0.43$ where the parallel spins of Cr^{III} and Ni^{II} are almost completely compensated by the antiparallel spins of Mn^{II}. For this reason, the experimental temperature dependences of magnetisation for the $(Ni^{II}_{0.38}Mn^{II}_{0.62})_{1.5}[Cr^{III}(CN)_6]\cdot 8H_2O$ phase coincided with the theoretical Neel curves: when measurements were carried out in an external field of 1000 G (stronger than the coercive field), the $J_s(T)$ dependences contained two maxima, while in an external field of 10 G (weaker than the coercive field) one maximum was observed and the curve intersected the abscissa axis (*i.e.* the magnetisation sign changed) at ~ 40 K. (It should be noted that at $x = 0$ or 1, the magnetisation of the specimens below the critical temperature increased monotonically as the temperature was decreased; these measurements were carried out in a field of 1000 G.) As a result, the magnetisation of a specimen at temperatures below 40 K was positive in an external magnetic field of $H > H_c$ and negative in a field of $H < H_c$.

Thus, it was shown [38, 39] that by varying the composition of a compound by chemical methods, it was possible to obtain phases in which the direction of the magnetic poles of the species was changed under the effect of an external magnetic field.

The critical temperatures of Prussian blue analogues capable of magnetic ordering can also be changed by electrochemical [40] or optical stimulation.[41] In the latter case, consecutive irradiation of, *e.g.*, $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$ with red ($\lambda = 660$ nm) and blue ($\lambda = 450$ nm) light at a sufficiently low temperature (5 K) made it possible to increase and then to decrease the magnetisation of the specimen; this is of undoubted interest for those engaged in the development of magnetic-optical memory blocks. Pioneer studies [40, 41] showed that the targeted selection of photosensitive hexacyanometallates can be carried out by molecular design. Japanese researchers implemented light-controlled inversion of magnetic poles on specimens of the mixed ferri-ferromagnet $(Fe_{0.4}Mn_{0.6})_{1.5}[Cr(CN)_6]\cdot 7.5H_2O$ [42] and developed a technology for growing thin coloured magnetic films of $(Fe^{II}_xCr^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]\cdot zH_2O$ on electrode surfaces.[43]

A principle for the synthesis of hexacyanometallates with high critical temperatures was suggested.[25, 30] It was found in studies of specific hexacyanometallate series that the synthesis of molecular ferromagnets (structural analogues of Prussian blue) should be based on ions of the first transition period metals (V^{II}, V^{III}, Cr^{II}), despite their small stability under ordinary conditions. Comparison of the magnetic properties of $Cs_2Mn^{II}[V^{II}(CN)_6]$ (see Ref. 30) with those of $CsMn^{II}[Cr^{III}(CN)_6]\cdot H_2O$ (see Refs 44 and 45) and $Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$, which are isostructural to the former, is indicative in this respect (see also Table 1).[46] All the three compounds contain Mn^{II} ions in the high-spin d^5 configuration in a weak ligand field (N_6-octahedral coordination environment) and metal ions in the d^3 configuration (V^{II}, Cr^{III} and Mn^{IV}) located in a strong ligand field (C_6-octahedral coordination environment).

The basic difference between the compounds of this period is that the energy of the t_{2g} orbitals for d^3 ions decreases with an increase in the element atomic number, *i.e.*, on going from V^{II} to Cr^{III} and then to Mn^{IV}. For example, the magnetic ordering temperatures of 125, 89.8 and 48.7 K for $Cs_2Mn^{II}[V^{II}(CN)_6]$, $CsMn^{II}[Cr^{III}(CN)_6]\cdot H_2O$ and $Mn^{II}[Mn^{IV}(CN)_6]\cdot 1.14H_2O$, respectively, show that the introduction of a d^3 transition metal ion with higher energies of the t_{2g} orbitals results in compounds with higher temperatures of the magnetic phase transition into the ferromagnetic state. In other words, the more effective the dative bonding of the bridging cyanide ligands due to bonding of their π^* orbitals the higher the energy of interaction between the spins of the neighbouring paramagnetic centres. In addition, the increase in the energy of exchange interaction between the unpaired electrons of the neighbouring paramagnetic centres is known to correlate with the increase in the magnetic ordering temperature.[47]

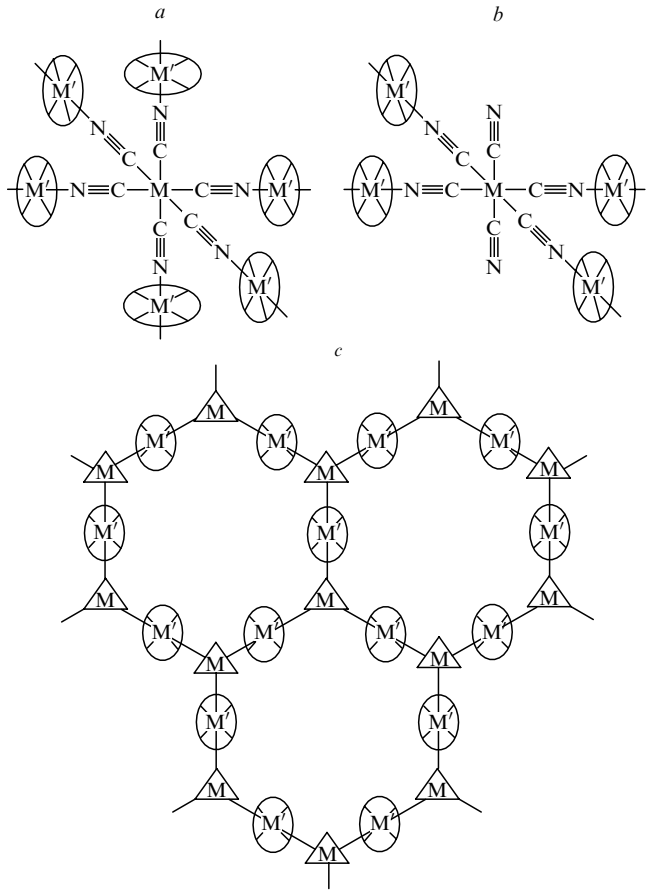
Unfortunately, it has to be noted that the technique for the synthesis of hexacyanometallates as single crystals of high quality, which is important for a detailed study of magnetic-structural relationships, has not been developed yet. As a rule, conclusions on the structure of compounds are based only on the analysis of powder diffractograms. In addition, all Prussian blue analogues with a cubic symmetry of the crystal structure do not manifest magnetic anisotropy.[48] These facts stimulated the synthesis of other cyanide complexes. Of the studies in this field, it is necessary to note the synthesis of the first paramagnetic tetrahedral cyanometallate $[Ph_3P=N=PPh_3]_2[Mn^{II}(CN)_4]$ the structure of which has been established completely.[49] Based on this compound, $Mn^{II}[Mn^{II}(CN)_4]$ having a interpenetrating diamond-like structure was obtained.[50] By itself, $Mn^{II}[Mn^{II}(CN)_4]$ is ordered antiferromagnetically, but the authors have a good reason to believe that representatives of the future family $M'[Mn^{II}(CN)_4]$ ($M' \neq Mn^{II}$), unlike $Mn^{II}[Mn^{II}(CN)_4]$, should have uncompensated spins and should behave as ferrimagnets below T_c. Single crystals of $Mn_2(H_2O)_5[Mo(CN)_7]\cdot 4H_2O$ (α-phase) and $Mn_2(H_2O)_5[Mo(CN)_7]\cdot 4.75H_2O$ (β-phase) were obtained by slow mutual diffusion of deoxygenated solutions of $K_4[Mo^{III}(CN)_7]\cdot 2H_2O$ and $Mn(NO_3)_2\cdot 6H_2O$ in a nitrogen atmosphere.[48] Both phases are monoclinic and have the same temperature of magnetic phase transition into the ferromagnetic state (51 K). The phases are unstable in air, but in special experiments it was possible to detect strong magnetic anisotropy on single crystals of the α-phase.

Thus, the transition from Prussian blue analogues with cubic structure to less symmetrical compounds has expanded the range of magnetically active polymeric cyanometallates with strong

anisotropy of magnetic properties. Compounds of this type are still rather rare, but their number increases gradually. A two-dimensional heptacyanomolybdate-based polymer, *viz*., $KMn_{1.5}(H_2O)_3[Mo(CN)_7]\cdot 3H_2O$ grown as single crystals,[51] and octacyanometallates $[M(CN)_8]^{3,4-}$, where M = Nb^{IV}, Mo^{V} or W^{V}, were reported at the Sixth Conference on molecular ferromagnets. The latter also undergo magnetic phase transition at rather high temperatures, *viz*., at ~40 K for $Cu_3[W(CN)_8]_2\cdot 3.4H_2O$ and at ~50 K for $Ni_3[W(CN)_8]_2\cdot nH_2O$.[52]

A problem in the design of molecular ferromagnets based on cyanometallates is that the cyano group, which is a bridging ligand, cannot be functionalised. As a matter of fact, this limits the possibilities of synthetic organic chemistry in the design of molecular magnets to the variation of the metal ions. The situation can be improved if some of the metal ions have previously been 'dressed in a coordination coat' in such a way as to reserve coordination sites for the approach of bridging cyanide groups. Certainly, the number of bonds between such metal ions and the bridging cyanide ligands is decreased, but the coordination environment acquires the possibility to affect the electronic structure of M′ and the steric structure (and hence the magnetic characteristics) of the compound as a whole. Scheme 1 shows the simplest versions of the formation of three- or two-dimensional polymeric structures with M and M′ ions alternating along different directions, *viz*., the framework motif (*a*),[53] the square (*b*)[54, 55] and the honeycomb (*c*) lattices.[56]

Scheme 1



M′ is a chelate matrix with a connectedness of 2; M is a hexacyanide fragment with a connectedness of 3;

In fact, the situation can turn out to be much more complex. In a hybrid version of the design of molecular ferromagnets based on a hexacyanometallate of one metal and a chelate of another,[54, 57, 58] the reaction of $K_3[Fe(CN)_6]$ with *trans*-$[NiCl_2(en)_2]$ (where en is ethylenediamine) gave the complex $[Ni(en)_2]_3[Fe(CN)_6]_2\cdot 2H_2O$, whose structure was characterised. It was found that in the solid phase, only three of the six cyanide ligands in the $Fe(CN)_6$ fragments participate in the formation of the bridging bonds with the Ni^{II} ions of the $Ni(en)_2$ fragments; 2/3 of the $Ni(en)_2N_2$ fragments contain a *cis*-coordinated Ni^{II} ion, while 1/3 contain a *trans*-coordinated Ni^{II} ion. As a result, in a crystal polymeric bands are extended along one of the crystallographic axes, while polymeric layers are formed along the other two directions. The interaction between the unpaired electrons in the $Ni^{II}-N\equiv C-Fe^{III}$ fragments, as in the usual hexacyanoferrate $Ni_3[Fe(CN)_6]_2$ (see Table 1), is of ferromagnetic character, and at temperatures below 18.6 K the complex $[Ni(en)_2]_3[Fe(CN)_6]_2\cdot 2H_2O$ undergoes a magnetic phase transition into the ferromagnetic state.

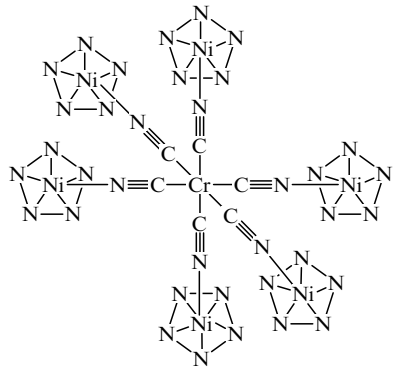
To date, a rather wide range of molecular ferromagnets of this group with various organic ligands have been studied. These include $PPh_4[Ni(pn)_2][M(CN)_6]\cdot H_2O$, $[Ni(pn)_2]_2[Fe(CN)_6]X$ and $[Ni(1,1\text{-dmen})_2]_2[Fe(CN)_6]X$, where M = Fe, Cr and Co, pn is 1,2-diaminopropane,[59] 1,1-dmen is 1,1-dimethylethylenediamine and $X = ClO_4^-, BF_4^-, PF_6^-, CF_3SO_3^-, BzO^-, I^-, N_3^-, NCS^-, NO_3^-$ (see Ref. 60) and $[Ni(tren)]_3[Fe(CN)_6]_2\cdot 6H_2O$, where tren is the tetradentate tris(2-aminoethyl)amine.[61] Using a classical macrocyclic ligand, 1,4,8,11-tetraazacyclotetradecane (cyclam), the following compounds: $[Ni(cyclam)]_3[Cr(CN)_6]_2\cdot 5H_2O$,[56] $[Ni(cyclam)]_3[Fe(CN)_6]_2\cdot 6H_2O$ and $[Fe(cyclam)][Fe(CN)_6]_2\cdot\cdot 6H_2O$, which are polymeric in the solid phase, have been synthesised and studied.[62] The efficiency of complexes of trivalent manganese with various polydentate Schiff's bases in the formation of heterometallic complexes with hexacyanometallates $[Mn(CN)_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ has been shown.[63–67] The critical temperatures range from 2 to 16.2 K for the group of compounds studied.

The $[Ni(bpm)_2]_3[Fe(CN)_6]_2\cdot 7H_2O$ complex, where bpm is bis(1-pyrazolyl)methane, with a rather high critical temperature has been synthesised and studied.[68] The solid phase of this compound is formed from pentanuclear heterometallic complexes $[Ni(bpm)_2]_3[Fe(CN)_6]_2$ linked into a diamond-like lattice by a system of hydrogen bonds involving molecules of crystallisation water. Although water molecules are generally poor conductors of exchange interactions,[69–72] high T_c (23 K) has been found for the $[Ni(bpm)_2]_3[Fe(CN)_6]_2\cdot 7H_2O$ phase. Dehydration of the compound results in the destruction of the structure and, as a consequence, in the loss of the magnetic ability. This situation is rather typical, *i.e*., the destruction of a system of hydrogen bonds forming a two- or three-dimensional structure of a compound results in the loss of the ability to undergo magnetic phase transition into the ferro- or ferrimagnetic state.[73, 74] However, it should not be considered that disintegration of a highly dimensional structure into separate polymetallic exchange clusters always results in zero-dimensional magnetic systems.

In recent years, studies in a specific area of the design of molecular ferromagnets, namely, large exchange clusters, is being developed intensely.[14, 75–78] Compounds of this type are nanoscale polynuclear molecular particles with a high degree of aggregation, such as $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4\cdot 2HOAc$, $Co_8O_4(PhCOO)_{12}(DMF)_4$, $NBu_4[Mn_8O_6Cl_6\cdot(PhCOO)_7(H_2O)_2]$ and $Fe_{11}O_6(OH)_6(PhCOO)_{15}$. Large polynuclear complexes arouse interest from the biochemical viewpoint as models of active polymetallic centres in enzymes.[79] On the other hand, despite the molecular nature of these compounds, the same effects as for the classical bulk magnets, including the original hysteresis loops that appear due to tunnelling effects between multiple spin conditions of different multiplicities, have been observed for them. One can find more details on the magnetic properties of these systems elsewhere, *e.g*., in Refs 80–88. Almost all of them contain polynuclear complexes with carboxylate, oxo and/or hydroxo bridging ligands.

A new possibility in the design of heterometallic polynuclear molecular complexes with the use of hexacyanometallates discussed above was shown.[24, 89] The reaction of $K_3[Cr(CN)_6]$ with

$[NiL(H_2O)](ClO_4)_2$, where L is tetraethylenepentamine, which blocks five coordination sites in the coordination sphere of Ni^{II}, resulted in $\{Cr[(CN)NiL]_6\}(ClO_4)_9$; its solid phase is formed by heptanuclear molecular exchange clusters $Cr^{III}Ni^{II}_6$ with ferromagnetic exchange interactions between the Cr^{III} and Ni^{II} ions.



One cannot rule out that new dendritic molecular magnets will be obtained from polynuclear compounds of this type.[90, 91]

The examples presented above show that the systematic development of methods for the synthesis of polymeric cyanide complexes with paramagnetic metal ions has made it possible to overcome, to a considerable degree, the above-mentioned 'drawbacks' inherent in the nature of Prussian blue analogues and, in addition, to contribute significantly to the supramolecular chemistry of metal cyanide complexes.[33, 92–100]

IV. M_3M' systems

1. Oxalates

The oxalate complexes of metals constitute the most representative group of molecular ferromagnets of the M3M′ class.[101–127] Okawa *et al.*[101–103] were the first to pay special attention to polymeric heterometallic oxalates. They chose these compounds taking into account the available data on polynuclear complexes with ferromagnetic exchange interactions between the unpaired electrons of the paramagnetic centres located on orbitals of different symmetries.[37, 104–108] It was thus desirable to obtain two- or three-dimensional heterospin structures 'pierced' by ferromagnetic pair exchange interactions (Fig. 1). It is absolutely unnecessary for a magnetic phase transition that all intra- and intermolecular exchange interactions be exclusively ferromagnetic; however, it should be noted that if only ferromagnetic exchange channels are present in the structure of a compound, higher values of magnetisation can be reached than in the case of antiferromagnetic interactions between unpaired electrons. The directed design of heterospin systems has made it possible to obtain[101–103] solid of $NBu_4[MCr(ox)_3]$ ($M = Cu^{II}$, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}) with magnetic ordering at 6–14 K (Table 2).

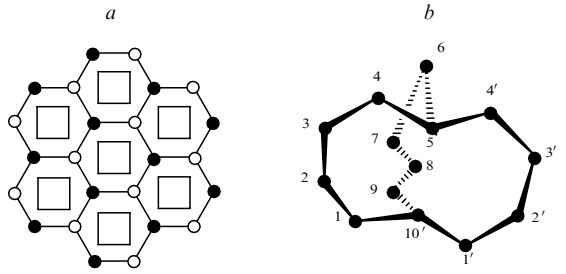


Figure 1. Scheme of the formation of a layered structure (*a*) and a fragment of framework structure with identical chiral centres (*b*); (*a*) 'honeycomb' motif; the light and dark circles indicate the alternating chiral (Λ and Δ) fragments of $M(ox)_3$ (ox is oxalate); the squares indicate the cavities that can be occupied by spacers (lacking counterions or solvent molecules);[102] (*b*) 'fused decagons' motif.[111, 117]

Table 2. Critical temperatures for oxalate complexes.

Compound	T_c /K	Structure dimensionality	Ref.
$NBu_4[Mn^{II}Cr^{III}(ox)_3]$	6	2D	102, 109
$NPr_4[Mn^{II}Cr^{III}(ox)_3]$	6	2D	114
$PPh_4[Mn^{II}Cr^{III}(ox)_3]$	6	2D	112
$NBu_4[Cu^{II}Cr^{III}(ox)_3]$	7	2D	101
$NBu_4[Co^{II}Cr^{III}(ox)_3]$	10	2D	102
$NBu_4[Fe^{II}Cr^{III}(ox)_3]$	12	2D	102
$NBu_4[Ni^{II}Cr^{III}(ox)_3]$	14	2D	102
$NBu_4[Cr^{II}Cr^{III}(ox)_3]$	–	2D	116
$PPh_4[Cr^{II}Cr^{III}(ox)_3]$	–	2D	116
$NBu_4[Ni^{II}Fe^{III}(ox)_3]$	28	2D	115
$NBu_4[Fe^{II}Fe^{III}(ox)_3]$	43	2D	115
$NBu_4[Mn^{II}Fe^{III}(ox)_3]$	49	2D	123
$N(C_5H_{11})_4[Mn^{II}Fe^{III}(ox)_3]$	27	2D	126
$[Co^{III}(bipy)_3][Co^{II}Co^{II}(ox)_3]ClO_4$	8	3D	122
$[Fe^{II}(bipy)_3][Co^{II}Co^{II}(ox)_3]$	6	3D	122
$[Ni^{II}(bipy)_3][Co^{II}Co^{II}(ox)_3]$	–	3D	122
$[Fe^{II}(bipy)_3][Fe^{II}Fe^{II}(ox)_3]$	–	3D	111
$[Cr^{III}(bipy)_3][Na^{I}Cr^{III}(ox)_3]ClO_4$	–	3D	120
$[Cr^{III}(bipy)_3][Mn^{II}Mn^{II}(ox)_3]ClO_4$	–	3D	120
$[Cr^{III}(bipy)_3][Mn^{II}Mn^{II}(ox)_3]BF_4$	–	3D	120
$[Co^{III}(bipy)_3][Na^{I}Cr^{III}(ox)_3]PF_6$	–	3D	120
$[Ni^{II}(phen)_3][Na^{I}Co^{III}(dto)_3]\cdot C_3H_6O$	–	3D	120
$[Ni^{II}(bipy)_3][[Mn^{II}Mn^{II}(ox)_3]$	–	3D	118
$[Fe^{II}(bipy)_3][Na^{I}Fe^{III}(ox)_3]$	–	3D	118
$[Fe^{II}(bipy)_3][Li^{I}Cr^{III}(ox)_3]$	–	3D	118
$[Fe^{II}(bipy)_3][Li^{I}Fe^{III}(ox)_3]$	< 3.5	3D	118
$NBu_4[Fe^{II}Ru^{III}(ox)_3]$	13	2D	127

Note. The following abbreviations are used: bipy is bipyridyl, phen is phenanthroline, and dto is dithiooxalate.

A three-dimensional framework structure was originally postulated for $NBu_4[MCr(ox)_3]$, although it was shown later[109–113] that these solids have layered honeycomb structures. One has to note the studies of $NBu_4[MnCr(ox)_3]$ single crystal,[109, 110] where strong anisotropy of the magnetic properties has been revealed. If measurements were made along the crystallographic axis *c*, which is perpendicular to the polymeric layers and coincides with the direction of the magnetic moments of Mn^{II} and Cr^{III}, the dependence of magnetisation on the magnetic field strength $M(H)$ was saturated in fields of $\sim$0.05 T. If the external magnetic field was oriented perpendicularly, *i.e.*, inside the nets of the polymeric layers, the $M(H)$ curve was far from saturation in the field of 10^4 G = 1 T. Later, a study of magnetic-structural relationships for $NPr^n_4[Mn^{II}Cr^{III}(ox)_3]$ and $NBu^n_4[Mn^{II}Fe^{III}(ox)_3]$ single crystals and a study of the magnetic structure in a neutron diffraction experiment with $[P(C_6D_5)_4][Mn^{II}Cr^{III}(ox)_3]$[114] powder confirmed that the magnetic properties of this type of subjects have strong anisotropy.

From the conceptual viewpoint, a series of studies[111, 117, 118] into the role of templates promoting the formation of either two-dimensional layered polymeric structures with a honeycomb motif (see Fig. 1 *a*) or three-dimensional frameworks with a motif of fused decagons (see Fig. 1 *b*) is important. The following principles for the construction of two- and three-dimensional polymeric oxalate structures were revealed: assembling a structure from various alternating distorted octahedral chiral (Λ and Δ) $M(ox)_3$

fragments results in polymeric layers with metal ions arranged in one plane, whereas assembling a polymeric structure from the same fragments of the same chirality gives a polymeric framework structure. As a whole, the two-dimensional honeycomb structure is achiral, and the distance between the layers is determined by the size of the cations located in the space between the layers. The three-dimensional structure formed from fused decagons is always chiral.

It was found that the $[XR_4]^+$ cations, where X = N or P and R = Ph, Pr, Bu or C_5H_{11}, favour the separation of two-dimensional honeycomb-like layered structures containing $[M^{II}M^{III}(ox)_3]_n^{n-}$, where M^{II} = V, Cr, Mn, Fe, Co, Ni, Cu, Zn; M^{III} = V, Cr, Fe, into the solid phase, while tris-chelated metals cations, *e.g.*, $[M(bipy)_3]^{2+/3+}$ (bipy is bipyridyl), cause the cross-linking of the polymeric anionic oxalate framework of $[M^{II}_2(ox)_3]_n^{2n-}$, $[M^{I}M^{III}(ox)_3]_n^{2n-}$ or $[M^{II}M^{III}(ox)_3]_n^{n-}$ into a three-dimensional framework of decagons.[117, 120] Another motif found in the solid phase of lanthanide-containing oxalates $[Ln^{III}Cr^{III}(ox)_3]\cdot nH_2O$ is composed of polymeric chains the shape of which resembles 'rope ladders'.[119] It was also found that framework structures similar to oxalates can also be obtained with the use of dithiooxalates (dto, see Table 2) as the bridging ligands.[120]

The progress of studies into the design of layered and framework molecular ferromagnets based on oxalate complexes has also stimulated interest in these compounds as a new type of microporous materials suitable for the separation of racemic mixtures and for directed asymmetric synthesis, as well as for catalysis. It has been shown for the layered polymeric microporous compound $Na_2(NMe_3Ph)_5[Cr(ox)_3]_2Cl\cdot 5H_2O$ that partial removal of the template from the compound by cation exchange at room temperature and even its complete removal by thermal treatment of the specimen accompanied by removal of water of crystallisation did not result in the loss of crystallinity.[121] This behaviour is similar to that of zeolite materials, therefore the phases under consideration can actually prove to be efficient for the separation of chiral subjects.

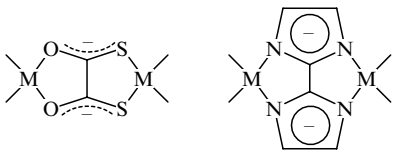
Compounds with high negative magnetisation of approximately the same magnitude as that of solid solutions of classical ferrospinels and the cyanide phases $(Ni^{II}_xMn^{II}_{1-x})_{1.5}.[Cr^{III}(CN)_6]\cdot 8H_2O$ discussed above, were described in Refs 124 and 125. The authors studied the specially selected series of layered polymeric oxalate complexes $A^I[M^{II}Fe^{III}(ox)_3]$, where $A^I = NPr^n_4$, NBu^n_4, $N(n\text{-}C_5H_{11})_4$, PBu^n_4, PPh_4, $NBu^n_3(C_6H_5CH_2)$, Ph_3PNPPh_3, $AsPh_4$; M^{II} = Mn, Fe, in which the interlayer distance can be adjusted by varying the cation A^I. Compounds with M^{II} = Fe behave as ferrimagnets with the ordering temperature of 33–48 K. For five of these compounds, transition from positive to negative magnetisation has been recorded at ~30 K in weak magnetic fields (~100 G). Such transitions are most characteristic of compounds with the highest critical temperatures. Moreover, characteristic changes were found in the series $N(n\text{-}C_nH_{2n+1})_4[Fe^{II}Fe^{III}(ox)_3]$, where n = 3–5. It was established that T_c increases with the interlayer distance; at low temperatures, magnetisation changes from positive for n = 3 to negative for n = 4 and 5.[125]

Single crystals of the layered polymeric heterometallic oxalate $N(n\text{-}C_5H_{11})_4[Mn^{II}Fe^{III}(ox)_3]$ could be grown and the anisotropy of its magnetic properties was studied.[109, 110, 114, 125] Studies into the anisotropy of the magnetic properties of single-crystal molecular ferromagnets are still rather rare, therefore they always arouse vivid interest. It was found[126] that $N(n\text{-}C_5H_{11})_4.[Mn^{II}Fe^{III}(ox)_3]$ with T_c = 27 K, as $NBu_4[MnCr(ox)_3]$ discussed above, has strong magnetisation anisotropy. The uncompensated magnetic moment directed perpendicularly to the plane of the polymeric layers (*i.e.*, in the same direction as in $NBu_4[MnCr(ox)_3]$) is rather small, *viz.*, 8.78×10^{-5} μ_B per magnetically active atom, which can be explained by the small angle of rotation of the magnetic sublattices (~0.001°) and the small difference between the *g*-factors of the d^5 metal ions.[126]

Table 2 lists the characteristics of a large group of polymeric metal oxalates, which allows some generalisations to be made. However, the overall picture for the understanding of the magnetic properties of compounds belonging to this class is still far from completion.[127, 128] Nevertheless, methods for directed synthesis of layered polymeric or framework polymeric metal oxalates have been developed to date, and it has become clear what the resulting chirality of the subjects would be and what spatial structure they would have. In addition, it is possible to adjust the distances between the layers in a series of layered compounds by varying the size of the cation A^I located in the interlayer space.[74, 121]

Experiments show that the highest magnetic ordering temperatures (~40–50 K) are reached if a compound contains a combination of metal ions having high spins (high-spin Mn^{II}, Fe^{II}, Fe^{III}), in accordance with the correlation $T_c \propto JS_1S_2$ (where S_1 and S_2 are the spins of the first and second paramagnetic centres, respectively). When metal ions are combined, it is possible to predict the temperature range in which the critical temperature of the expected compound will fall. Thus, the introduction of diamagnetic ions (for example, lithium or sodium ions) in polymeric oxalate systems leads to an increase in the distances between the paramagnetic centres, a reduction of the energy of exchange interaction between them and, hence, a sharp decrease in the critical temperature. On the other hand, the fact that the critical temperatures of the known framework oxalates (3D structures) are much lower than those of layered polymeric compounds (2D structures) requires a quantum-chemical explanation. The role of relativistic effects is not quite clear; the necessity of taking them into account in the description of the magnetic properties of heterometallic polymeric oxalates containing paramagnetic 4*d*- or 5*d*-metal ions was pointed out in Ref. 127. Such properties appear due to a significant spin-orbital interaction in these elements.

It may seem that the design of oxalate systems is limited only to the replacement of metal ions and template cations. This is hardly true. Certainly, oxalate polymers are the basic systems for the synthesis of the M3M′ class ferromagnets. On the other hand, current studies encourage a wider use of various diamagnetic and paramagnetic ligands which are structural analogues of the oxalate anion and hence favour the development of the synthesis of new molecular magnets. For example, the aforementioned dithiooxalate,[120, 129, 130] imidazoles,[131] imidazoleacetate[132] and biimidazole[133] may be regarded as such ligands.



In addition, investigations into the design of polynuclear mixed-ligand compounds, in which not all but only one or two ligands are oxalates,[134, 135] are certainly of interest. For example, the structure of complexes $M^{II}_2(dpm)(ox)_2\cdot xH_2O$, where M = Mn, Cu; x = 6, 5, respectively, and dpm is bipyrimidine (Fig. 2),[135, 136] is topologically identical with the honeycomb structure of layered polymeric oxalates (see Fig. 1 *a*). The way of self-organisation of three-dimensional frameworks upon formation of mixed-ligand complexes with an oxalate anion and bipyridyl has been studied.[137] Thus, addressing mixed-ligand complexes is also promising in the design of new molecular ferromagnets.

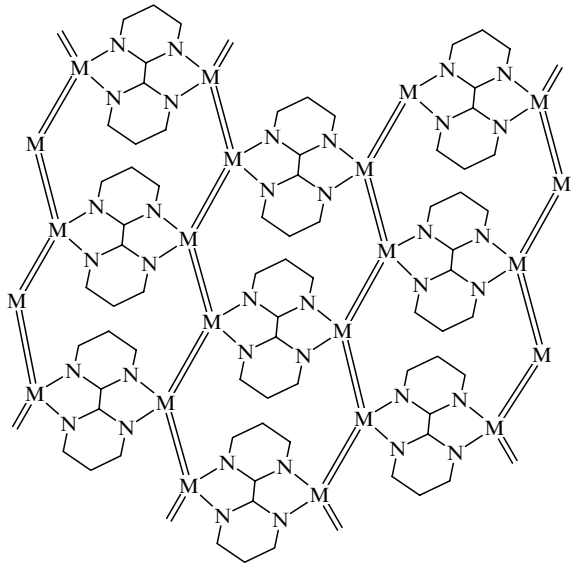
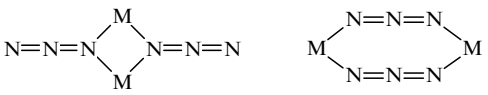


Figure 2. Scheme of a layered polymeric structure ('honeycomb' motif) of $M^{II}_2(dpm)(ox)_2 \cdot xH_2O$ [135, 136] and $M^{II}_2(dpm)(N_3)_4$.[138–140]
The double lines indicate the bridging oxalate or azide anions connecting the metal ions into chains, which are, in turn, linked by the bridging bipyrimidine ligands into layers.

2. Azides

The above approach to the synthesis of layered polymeric compounds based on mixed-ligand complexes of metal oxalates with bipyrimidine, but with the use of azide ligands instead of oxalate ones, has been developed further.[138–140] The authors succeeded in synthesising and studying a series of layered polymeric complexes with composition $M_2(N_3)_4(dpm)$, where M = Co^{II}, Fe^{II} and Mn^{II}. The structural motif of polymeric honeycomb-like layers in $M_2(N_3)_4(dpm)$ is exactly the same as that in $M^{II}_2(dpm)(ox)_2 \cdot xH_2O$ (see Fig. 2) with only one difference: the role of a bridge is played by two bridging μ-(1,1)-azide ligands instead of the oxalate anion, *i.e.*, according to the systematics accepted, the $M_2(N_3)_4(dpm)$ complexes correspond to the M3(1)M′ class. The authors believed that the introduction of the azide anion into polymeric structures would be expedient for obtaining polymers with exchange interactions alternating in sign (ferromagnetic–antiferromagnetic). As a rule, strong antiferromagnetic exchange interaction (−200 to −400 cm^{-1}) predominates in exchange clusters linked by a bridging oxalate anion or bipyrimidine.[13, 141, 142] However, it is known that in binuclear exchange clusters linked by azide following the μ-(1,3) pattern, the exchange interaction is antiferromagnetic,[143] while in those linked following the μ-(1,1) pattern, it is ferromagnetic.[144, 145–162]



μ-(1,1) μ-(1,3)

Experimental studies of the magnetic properties of the $M_2(N_3)_4(dpm)$ complexes have shown that competition between ferro- and antiferromagnetic exchange interaction channels does exist in them, and at low temperatures (< 12 K) these compounds behave as metamagnets with high critical magnetic fields (> 2 T).[138] It should be noted that the ferromagnetic character of exchange in μ-(1,1) type binuclear azide exchange clusters was confirmed by quantum-chemical studies of the $[M(\mu\text{-}1,1\text{-}N_3)_2M]$ and $[M(\mu\text{-}1,1\text{-}N_3)_3M]$ fragments, where M = Cu^{II}, Ni^{II}, Mn^{II} (see Ref. 146). For example, for the copper complex, the results of calculation for the distribution of spin density qualitatively agree with the experimental results of a polarised neutron diffraction study. The spin density distribution obtained in the calculated model is a superposition of the electron delocalisation and spin polarisation effects: delocalisation of unpaired electrons from the $d_{x^2-y^2}$ orbitals to the donor atom of the ligand decreases in the series Cu > Ni > Mn, while spin polarisation in the same series increases because of the increase in the number of unpaired electrons.[146] It was also found that the exchange is hardly affected by deviations of the uncoordinated azide ligand from the plane of the M(μ-N)(μ-N)M fragment, which opens the possibilities for a more flexible and versatile design of highly dimensional structures with the μ-(1,1) bridging azide.

In the synthesis of a layered polymer $Ni(N_3)_2L$, where L is 2,2-dimethylpropane-1,3-diamine,[163, 164] advantage was taken of the diversity of coordination capabilities of the N_3^- ligand known for polynuclear complexes with azide ligands.[147–157] The bidentate ligand was shown not to participate in the formation of bridging bonds. The layered polymeric structure is formed by only the azide anions, some of them serving as μ-(1,1) bridges and others as μ-(1,3) bridges. The magnetic ordering temperature for $Ni(N_3)_2L$ was found to be rather high (T_c = 55 K), although the residual magnetization at 4.2 K is very low (6×10^{-3} μ_B). Below the critical temperature, this compound behaves as a weak ferromagnet, but the reason why the weak ferromagnetism appeared (antisymmetric exchange[165–168] or *g*-factor anisotropy of the nickel ion[169]) remains obscure.

Similar magnetic behaviour has been recorded for a series of layered polymeric coordination compounds $Mn(N_3)_2L_2$, where L stands for monodentate ligands, *e.g.*, pyridine, 3-acetylpyridine, 4-acetylpyridine, 4-cyanopyridine or ethylisonicotine.[170–172] In polymers with exclusively μ-(1,3) bridging function of the azide ligand, antiferromagnetic exchange interactions between the manganese ions occur, whereas in polymers with alternating μ-(1,1) and μ-(1,3) bridging azides, alternation of ferromagnetic and antiferromagnetic channels of exchange interaction is observed. At low temperatures (< 16–40 K) the ESR signal from polycrystalline specimens broadens and compounds behave as weak ferromagnets with small magnetic moments.[172]

3. Dicyanamides

The first reported molecular ferromagnets[173–178] were based on polymeric dicyanamide derivatives of transition metals $(ML_2)_\infty$, where L = $N(CN)_2^-$; M = Co, Ni. In solid $(ML_2)_\infty$, each ligand has tridentate bridging coordination (Fig. 3 *a*).

Each $N(CN)_2^-$ bridging ligand is bound to metal ions through two terminal nitrogen atoms of the nitrile groups and the central amide nitrogen atom. In turn, each metal ion is bound to six different $N(CN)_2^-$ ligands, four of which are coordinated by the nitrile nitrogen atoms and two are coordinated by the amide nitrogen atoms. This results in a framework structure similar to that of rutile. These compounds undergo magnetic phase transition into the ferromagnetic state at 9 (Co) and 20 K (Ni). An important result of these studies is that no ordering effects were detected down to 2 K for the isostructural compound $(CuL_2)_\infty$ characterised by the pronounced Jahn–Teller effect, which is inherent in Cu^{II}. $(CuL_2)_\infty$ behaves as a usual paramagnet over the entire measurement range. In our opinion, this behaviour is due to a considerable elongation of the bonds between the copper ions and the amide nitrogen atoms in the structure of $(CuL_2)_\infty$,[173] *i.e.* the magnetic structure consists of the chains $[-Cu-(N\equiv C-N-C\equiv N)_2-Cu-(N\equiv C-N-C\equiv N)_2-]_\infty$ with Cu^{II} ions that weakly interact through five bridging atoms (Fig. 3). As regards the magnetism, $(CuL_2)_\infty$ belongs to the M5M′ class rather than to M3M′ as is the case for $(CoL_2)_\infty$ and $(NiL_2)_\infty$. Band chains of this type with weakly interacting manganese ions, $[-Mn-(N\equiv C-N-C\equiv N)_2-Mn-(N\equiv C-N-C\equiv N)_2-]_\infty$, have been reported.[179] They were detected for solid $MnL_2(CH_3OH)_2$, which confirms the assumption stated above.

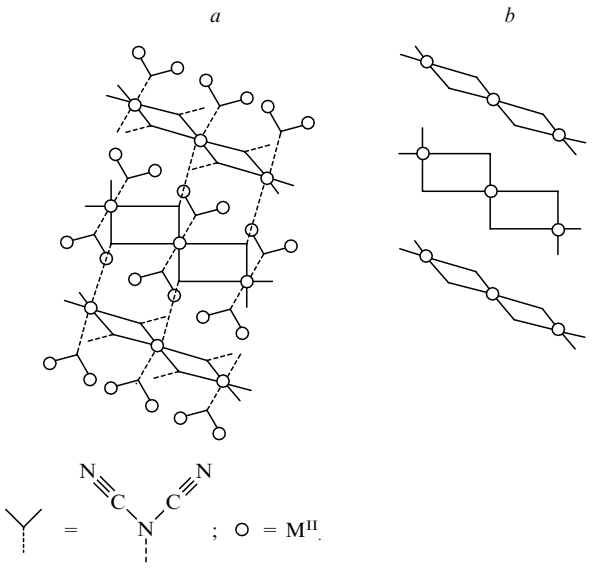


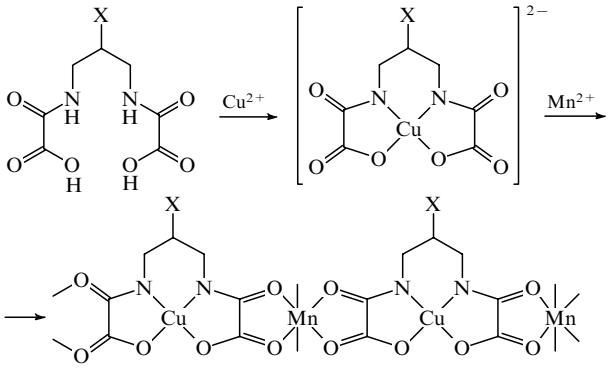
Figure 3. Scheme of decomposition of a three-dimensional framework structure of $(ML_2)_\infty$ (*a*) into separate chains (*b*) upon increase in the metal–amide nitrogen atom distance.

Experiments with the use of neutron diffraction on $(ML_2)_\infty$ powders (M = Co, Ni, Mn) and measurements of specific heat capacity of these compounds in the region of magnetic phase transition were carried out.[176–178] It was possible to determine correctly the Curie temperatures for the ferromagnets, *viz*., cobalt (8.7 K) and nickel (19.7 K), the Neel temperature for an antiferromagnet $(MnL_2)_\infty$ (16 K), to determine the magnetic structure of the compounds and to establish that $(CoL_2)_\infty$ exists as two polymorphic modifications, one of which (α) can undergo ferromagnetic ordering below the critical temperature. In the studies of the magnetic properties of $(ML_2)_\infty$ (M = Fe, Co, Ni) and alloys $[Ni_{0.5}Co_{0.5}L_2]_\infty Ni(OH)_{2-x}L_x$, some unusual properties of these compounds were reported.[180, 181] First, an increase in the pressure to 17 kbar makes it possible to increase the critical temperature of the phase by $\sim$10%; this is an important feature of molecular ferromagnets that rather commonly have a 'loose' structure. Second, anomalously high coercive fields are characteristic of the molecular ferromagnets studied: 710, 7975 and 17 800 Œ, respectively, for the nickel, cobalt and iron complexes.[182–184] The latter value is not only the highest in the series of molecular ferromagnets but also exceeds the coercive fields for Sm–Co and Re–Nd–B alloys (the coercive field for classical magnetically hard materials reaches 10^3–10^4 Œ).[182]

Thus, the examples presented above show that the organic dicyanamide anion can be efficiently used in the design of molecular ferromagnets.

4. Dioxamates

An original approach to the design of polymeric heterospin systems based on mixed-ligand complexes with polydentate ligands was developed.[185–195] The construction of these systems is a multistage directed design of molecular ferromagnets starting from the synthesis of a specific polyfunctional ligand (various dioxamates) and allowing one to obtain a solid heterospin layered polymer with a strictly determined alternation of paramagnetic centres. In the first stage, a complex of Cu^{II} with a tetradentate ligand is formed, and then cross-linking of copper-containing fragments into a chain occurs through the formation of chelate complexes of Mn^{II} with the oxygen atoms of the oxamate groups. The Mn^{II} ion cannot compete with Cu^{II} for the donor nitrogen atoms, as its thermodynamic constants of complex formation with



X = H, OH.

nitrogen-containing ligands are much smaller than those for copper. As a result, a chain with regular alternation of Cu^{II} and Mn^{II} is formed.

Mutual arrangement of the paramagnetic centres belonging to different chains is an essential factor. It was found[185–187] that in the case of *N*,*N*′-propane-1,3-diyldioxamate (X = H), the Cu^{II} ions in solid $MnCuL \cdot 5H_2O$ are arranged above Cu^{II} ions, while the Mn^{II} ions are above Mn^{II} ions; the magnetic moments of ions belonging to different chains are oriented oppositely (due to the predominant antiferromagnetic exchange interactions) and compensate each other (Fig. 4 *a*). The magnetic moments in the copper and manganese sublattices generally tend to compensate each other. As a result, the compound is ordered antiferromagnetically at low temperature (T_c = 2.2 K).

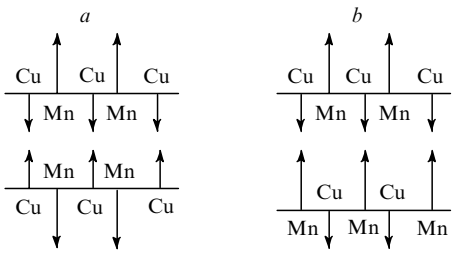
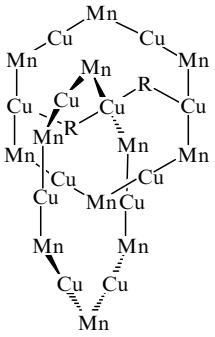


Figure 4. Antiferromagnetic spin ordering of neighbouring chains with resulting zero (*a*) and non-zero (*b*) magnetic moment.

In an attempt at changing the mutual arrangement of the metal ions, the authors synthesised the $MnCuL' \cdot 3H_2O$ complex, where L′ is *N*,*N*′-(2-hydroxypropane-1,3-diyl)dioxamate (X = OH). In the solid phase of this compound, the chains $(...Cu...Mn...)_\infty$ are shifted relative to each other in such a way that the OH groups of one chain form hydrogen bonds with the water molecules coordinated by the Mn^{II} ions of the other chain. As a result, a staggered arrangement of the Cu^{II} and Mn^{II} ions appears (Fig. 4 *b*). The magnetic moments of ions from different chains tend to be oriented oppositely. However, in this case each Cu–Mn pair forms a difference magnetic moment, and on the whole, uncompensated magnetic moment of the manganese and copper sublattices appears, as inside these sublattices all spins are oriented in the same way. As the temperature is decreased, the $MnCuL' \cdot 3H_2O$ structure is ordered ferromagnetically (T_c = 4.6 K). A series of molecular ferromagnets with the Curie temperatures of 5–22 K were obtained using this approach.[188–193] The antiferromagnetic character of exchange interaction between the neighbouring Cu^{II} and Mn^{II} ions in these compounds was confirmed by polarised neutron diffraction.[194]

A method for the synthesis of the multispin compound $R_2Mn_2(CuL)_3(DMSO)_2 \cdot 2H_2O$, where R is the 2-imidazoline 1-oxyl 3-oxide-containing radical cation; L is the *o*-phenylene-

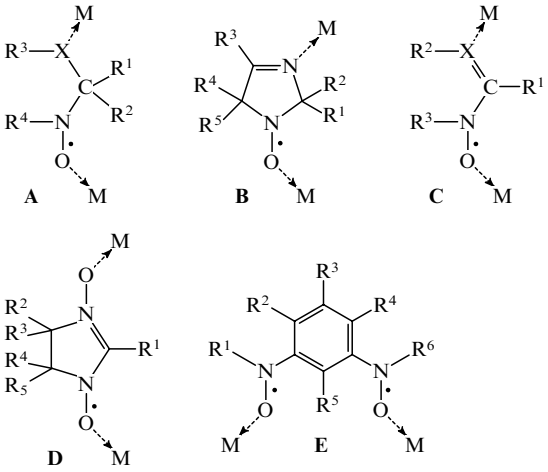
dioxamate anion, was developed.[196, 197] The structure of the compound consists of a system of almost perpendicular (73°) interlocked networks analogous to those of layered polymeric oxalates (see Fig. 1 *a*), the only difference being that the vertices of each hexagon are occupied by the Mn^{II} ions, while the midpoints are Cu^{II} ions.

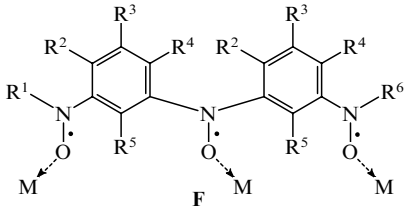


The tetradentate ligands L play the role of bridges connecting Mn^{II} and Cu^{II}. Each of the oxygen atoms of the nitronyl nitroxide is coordinated by Cu^{II} ions from different networks, which results in the formation of additional polymeric chains in the crystal; the compound is ordered as a ferrimagnet below 22.5 K. Using this approach, the authors obtained a series of molecular ferromagnets $(R\text{-}Rad)_2M_2(CuL)_3$, where R-Rad is the 2-(4-*N*-alkylpyridinium)-4,4,5,5-tetramethyl-2-imidazoline 1-oxyl-3-oxide cation, M = Mn^{II}, Ni^{II}, Co^{II}, with critical temperatures in the range of 22–37 K.[198]

V. M4M′, M5M′ and M7M′ systems

In the Introduction, we discussed the importance of involvement of synthetic organic chemistry in the design of molecular ferromagnets. However, in the classes of compounds considered above, it is not always possible to attach additional functional groups to the bridging ligand atoms. Besides, simple elongation of the hydrocarbon chain will result in a sharp decrease in the energy of exchange interactions between the unpaired electrons of the paramagnetic centres. To resolve the situation, one can use stable nitroxides; the methods for their synthesis and modification are well developed (see, *e.g.*, Ref. 11). The bridging heterospin structures are shown below. Depending on the nature of the group X, these systems can contain a minimum of four atoms in the bridge. Fragments of bridging structures representing derivatives of stable 2-imidazoline[199–214] and 3-imidazoline[215–227] nitroxides and acyclic polynitroxyls linked through benzene or heterocyclic rings are also shown.[12, 228–231]

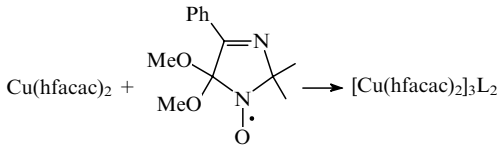




Substituents R^n in nitroxides may be varied over a broad range. The presence of one or several $>N^{\cdot}\!-O$ groups (preferrably, with the greatest possible delocalisation of spin density over the bridging organic fragment) makes it possible to maintain efficient exchange interactions between the unpaired electrons of the metal ions and the nitroxyl radicals.

A group of chain polymers based on mixed-ligand complexes of Mn^{II} and Ni^{II} hexafluoroacetylacetonates with nitronyl nitroxides (structure D) and capable of ferrimagnetic ordering at $T < 8$ K has been reported for the first time in Refs 232–235. The solid phases formed by polymeric chains of $[Mn(hfacac)_2L]_\infty$, where hfacac is hexafluoroacetylacetonate and L represents polynitroxyls, are characterised by similar ordering.[236, 237] Studies of these subjects led to the conclusion that, despite the strong intrachain exchange (the integral of exchange interaction is greater than 250 cm^{-1}),[234] one cannot hope to obtain ferromagnets with high Curie temperatures from these compounds due to the very low energies of intermolecular exchange interactions. However, the design of molecular magnets makes it possible to pass from chain structures to structures with higher dimensionality.

In particular, synthesis of a series of triradicals with structures of the **F** type has been developed. High conformational mobility of acyclic nitroxyl fragments linked by single bond to an aromatic ring enabled the realisation of a framework structure in the complex $[Mn(hfacac)_2]_3L_2$ (L is a triradical; R^2, R^4, R^5 = H; R^1, R^3, R^5 = Bu^t), which is ordered as a ferrimagnet at 46 K.[238–240] Each coordination matrix $[Mn(hfacac)_2]$ is bound to two ligands, whereas each ligand is surrounded by three different $Mn(hfacac)_2$ units. Nevertheless, it should not be thought that a framework polymer is always formed at the stoichiometric ratio $M(hfacac)_2$: nitroxyl = 3 : 2. We found that this composition can also be observed for specific trinuclear molecules with radicals[241] which are formed particularly often in the synthesis of mixed-ligand complexes of $Cu(hfacac)_2$ with nitroxides (Fig. 5).[204, 209, 219, 221, 242]



If the compounds have the same composition, one has to pay special attention to the possibility of formation of polymorphic modifications, as their magnetic properties can differ considerably.[199, 222, 232, 243, 244]

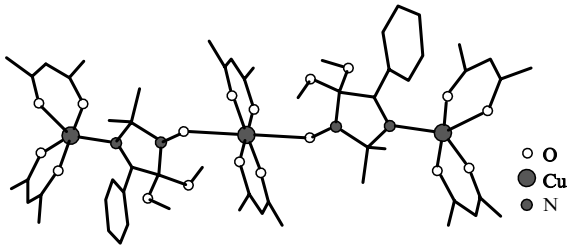
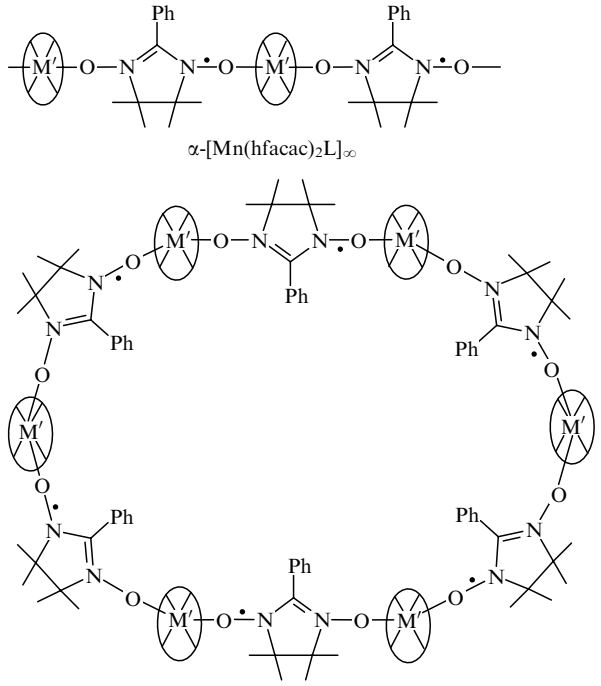


Figure 5. Molecular structure of the complex $[Cu(hfacac)_2]_3L_2$.

Scheme 2



Scheme 2 shows that *trans*-coordination of the bridging 2-imidazoline nitronyl nitroxyl ligands in $Mn(hfacac)_2$ results in the formation of polymeric chains (α) in the solid which undergoes three-dimensional magnetic ordering below 6 K.[232] *cis*-Coordination of radicals results in hexanuclear separate molecules (β) due to closure of a 36-membered macrocycle formed by the manganese atoms and the O–N–C–N–O fragments of the paramagnetic ligand.[199]

The ground state of hexanuclear molecules is that with $S = 12$ in the temperature range from 5 to 300 K; the β-modification behaves as an ordinary paramagnet.

The bischelate of divalent nickel with acetonyl 3-imidazoline nitroxide derivative NiL_2 (Fig. 6) also exists as two polymorphic modifications (α and β).[222] Both modifications have layered polymeric structures. The goffered layered structure of the solid is formed owing to coordination of the nitroxyl oxygen atoms of the neighbouring bischelates by the nickel ion. The coordinated oxygen atoms of the nitroxyl groups are *trans*-coordinated in the α-modification and *cis*-coordinated in the β-modification. In solid α-NiL_2, the antiferromagnetic exchange interactions between the unpaired electrons of the paramagnetic centres in the $>N\dot{-}O-Ni^{II}-O\dot{-}N<$ fragments predominate, and μ_{ef} approaches zero as the temperature is lowered. In β-NiL_2, the antiferromagnetic ($J \simeq -115\ cm^{-1}$) and ferromagnetic ($J \simeq 10\ cm^{-1}$) exchange compete, which results in antiferromagnetic ordering at $T_c = 14$ K (Fig. 7).

Taking into account the stereochemical non-rigidity of bischelates of the NiL_2 type, it is possible, by selecting the crystallisation conditions, to obtain modifications having either a molecular structure incapable of cooperative magnetic ordering or a layered polymeric structure that displays a tendency towards cooperative magnetic ordering.[243, 245]

Perhaps, the only factor that limits the possibilities of the design of molecular ferromagnets from complexes with nitroxyl radicals is that the $>N\dot{-}O$ group, which results from the oxidation of the corresponding hydroxylamine, is a weak donor of electron density. However, coordination of the nitroxyl group or any other way of its inclusion in the network of polymeric exchange channels are necessary for cooperative magnetic ordering.[220] Therefore,

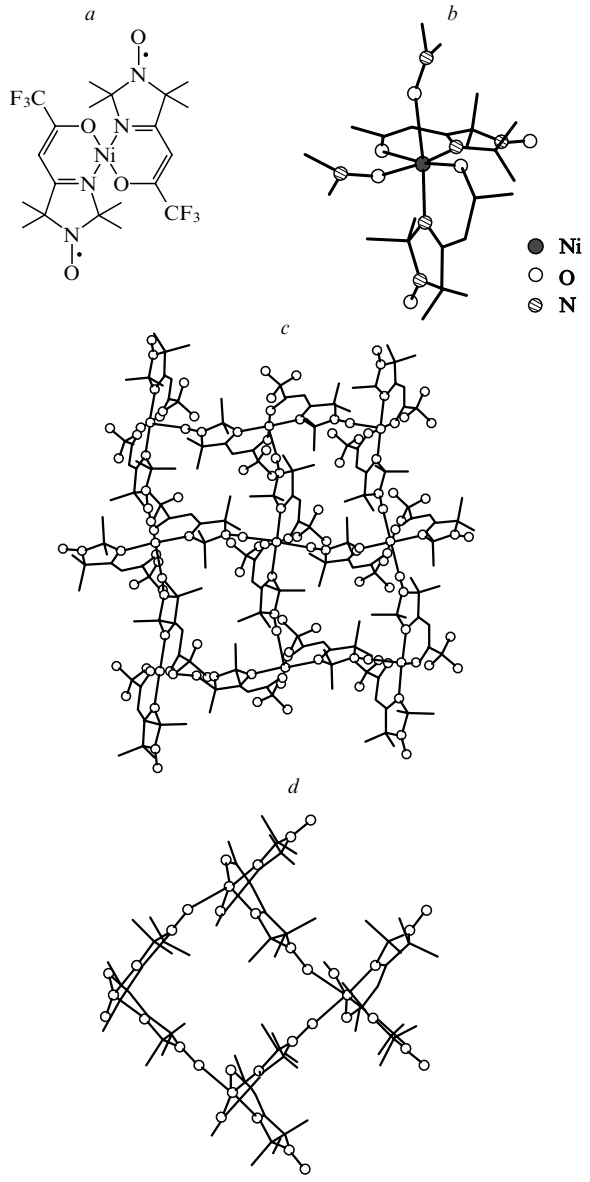


Figure 6. Fragments of layered polymeric structures of α- and β-NiL_2; (*a*) NiL_2 complex; (*b*) coordination of the Ni atom in β-NiL_2; (*c*) layered polymeric structure of α-NiL_2; (*d*) layered polymeric structure of β-NiL_2.

metal hexafluoroacetylacetonates have mostly been used as acceptor matrices in early studies of heterospin systems based on complexes of transition metals with stable nitroxides.[7, 11] It was shown[246] that fluorinated carboxylates of metals can be used instead of hexafluoroacetylacetonate matrices; heterospin compounds capable of magnetic ordering at 21–24 K were obtained from mixed-ligand complexes of manganese bis(pentafluorobenzoate) with 2-imidazoline nitroxide.

It is possible in principle to get rid of the 'ballast' diamagnetic anionic ligands, such as hexafluoroacetylacetonate or carboxylate, if the organic radical is originally constructed in such a way that it can play both the roles of a bridge and an anion. We succeeded in synthesising a vast group of molecular ferromagnets of this type with layered polymeric or framework structure (Table 3). Scheme 3 illustrates the formation of polymeric layers in heterospin bischelates based on complexes of transition metals with derivatives of the stable 3-imidazoline nitroxide.

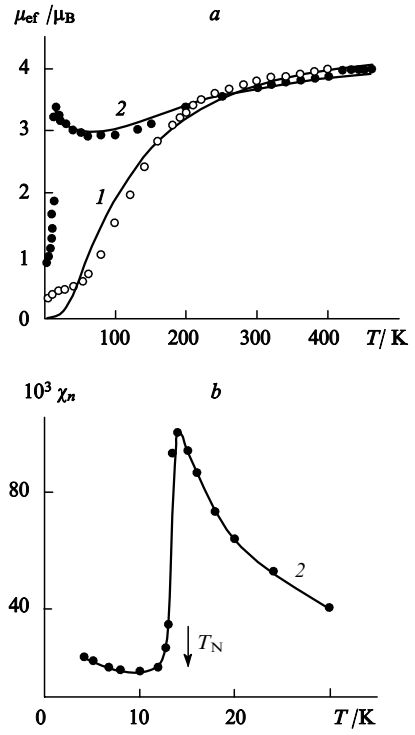
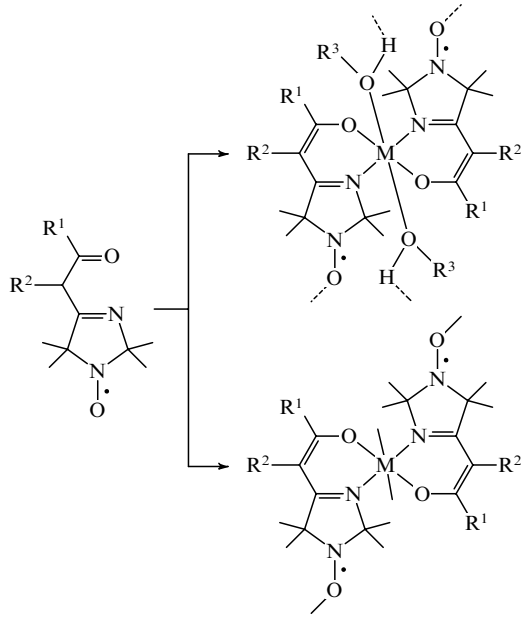


Figure 7. Temperature dependences of the effective magnetic moment for α- (*1*) and β-NiL_2 (*2*) (*a*) and the specific magnetic susceptibility (χ_n) for β-NiL_2 (*b*).

Scheme 3



R^1 = CF_3, COOMe, COOEt; R^2 = Me, H, Cl, Br; M = Cu, Ni, Co.

High-quality single crystals of intracomplex chelates can be obtained from various organic solvents; therefore, it was possible to determine the crystal and molecular structures for all of the heterospin compounds listed in Table 3. A distinctive feature of the composition of the compounds studied is the presence of non-crystallisation molecules of alcohols in the crystal. In the solid phase, the metal ion coordinates the oxygen atoms of the OH groups belonging to two ROH fragments, then the $ROH-ML_2-HOR$ groups are linked by hydrogen bonds $ROH\cdots O\doteq N\lesssim$ with two neighbouring $ROH-ML_2-HOR$ units. As a result, the bridging alcohol molecules 'cross-link' the

Table 3. Magnetic ordering temperatures for complexes with 3-imidazoline nitroxyl radicals.

Compound	T_c /K	Structure dimensionality	Ref.
$R^1 = CF_3$, $R^2 = H$			
$NiL_2(MeOH)_2$	6.5	2D	247, 250
$NiL_2(H_2O)_2$	–	2D	72
$NiL_2(EtOH)_2$	5.3	2D	247, 250
$NiL_2(C_3H_5OH)_2$	6.2	2D	248
$NiL_2(Pr^nOH)_2$	6.0	2D	248
$NiL_2(Bu^nOH)_2$	5.9	2D	249
$NiL_2(Bu^iOH)_2$	4.8	2D	249
$NiL_2(n\text{-}C_5H_{11}OH)_2$	6.3	2D	248
$NiL_2[HO(CH_2)_4OH]$	6.8	3D	247
$NiL_2[HO(CH_2)_5OH]$	4.0	3D	247
$CoL_2(MeOH)_2$	7.1	2D	251
$CoL_2(EtOH)_2$	8.1	2D	11, 248
$CoL_2[HO(CH_2)_4OH]$	4.0	3D	249
CuL_2	–	molecular	254, 255
$R^1 = CF_3$, $R^2 = Cl$			
$NiL_2(MeOH)_2$	5.0	2D	252
$CoL_2(MeOH)_2$	7.1	2D	252
CuL_2	5.0	2D	253
$R^1 = CF_3$, $R^2 = Me$			
$NiL_2(MeOH)_2$	5.8	2D	252
$R^1 = COOEt$, $R^2 = H$			
CuL_2	4.2	2D	253
$R^1 = COOMe$, $R^2 = H$			
CuL_2	5.0	2D	253
$R^1 = COOEt$, $R^2 = Br$			
CuL_2	4.3	2D	253

ML_2 fragments to form polymeric layers (monohydric alcohols) or a three-dimensional framework (dihydric alcohols), *i.e.* the two- or three-dimensional structure is formed by hydrogen bonds.[247, 248, 250–253]

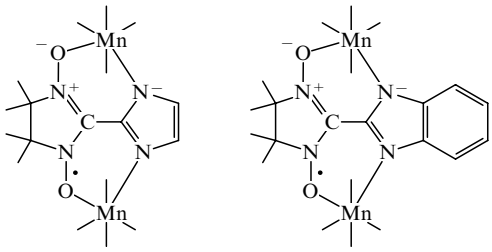
It should be noted that a separate metal ion in $ML_2(ROH)_2$ is surrounded by a large number of 'organic' atoms (C, H, N, O). For example, there are 90 C, H, N and O atoms altogether per each Ni^{II} ion in $NiL_2(n\text{-}C_5H_{11}OH)_2$; in spite of this, the compound is capable of cooperative magnetic ordering at low temperature. Removal of the alcohols and transition to layered polymeric structure in solid ML_2 leads to the loss of its ability to undergo ferromagnetic ordering.[222, 248] At first glance, this seems paradoxical, as the transition from ML_2 to $ML_2(ROH)_2$ is accompanied by an abrupt increase in the fraction of the organic component in the compound, and hence, a decrease in the number of paramagnetic centres per unit volume of the solid phase of the complex. Nevertheless, it is such changes that determine the ability to undergo magnetic phase transition typical of weak ferrimagnets.[247]

It was found by comparison of the magnetic properties of the isostructural complexes $NiL_2(ROH)_2$ and $NiL_2(H_2O)_2$ (see Ref. 72) that the introduction of water molecules in the exchange channel $\gtrsim N\doteq O\cdots HOH-M^{II}-HOH\cdots O\doteq N\lesssim$ results in a sharp decrease in the exchange interaction energy and, hence, the loss of ability to undergo magnetic phase transition, despite the structural identity of the exchange channels in $NiL_2(H_2O)_2$ and $NiL_2(ROH)_2$. The high kinetic stability of complexes with alcohols, especially dihydric ones, was noted. For example, no changes in the composition and properties of $NiL_2(MeOH)_2$ and

$NiL_2[HO(CH_2)_4OH]$ were recorded upon their storage under normal conditions for 10 years. Large single crystals (with sizes from several millimetres to two centimetres) of many compounds of this series are also storage-stable. The possibility of obtaining complexes of transition metals with nitroxyl radicals in the form of sufficiently large single crystals makes them convenient subjects for studying the anisotropy of the magnetic properties[233–235, 238, 245, 247] and the spin density distribution using polarised neutron diffraction.[256–259] For example, Fig. 8 shows the results of a study of the magnetisation anisotropy for $NiL_2(MeOH)_2$ and $NiL_2(EtOH)_2$ and demonstrates the relation between the direction of easy magnetisation axis for single-crystal $NiL_2(EtOH)_2$ as a macrosubject and the direction of the second-order crystallographic axis of the crystal microstructure. The coincidence of these directions is a prerequisite (within the framework of the classical magnetism concept) for single crystals belonging to the space group $P2_1/c$.[168]

It was established in systematic studies of transition metal complexes with stable 3-imidazoline nitroxides that the structural dimensionality of a solid can be controlled by varying the substituents R^1 and R^2 in the side chain of the ligand. If R^1 is not an electron density acceptor (alkyl, aryl), the solid phase of the complex has a molecular structure with a square or tetrahedral environment of the metal ion. If R^1 is a strong electron density acceptor (for example, CF_3, COOEt), the central metal ion coordinating the donor atoms of the neighbouring molecules also becomes a strong acceptor. The coordination number of the central ion is completed to 6 and a layered polymeric structure is formed.[72, 260] In the case where the acceptor ability of a metal ion attained only due to the introduction of an electrophilic substituent R^1 is insufficient to implement a two-dimensional solid state structure, the introduction of additional acceptor groups, for example, halogen atoms, as the substituent R^2 is effective.[253]

In the examples of heterospin complexes discussed above, the 3-imidazoline nitroxyl radical plays the role of a tridentate bridge. Recently, heterospin layered polymers with deprotonated nitronyl nitroxyl radicals (NIT) containing an imidazole (Im) or benzoimidazole (BzIm) substituent at position 2 of the paramagnetic heterocycle were described.[261, 262]



Such substituents perform the tetradentate bridging function (M53M′ systems). Complexes with composition $[Mn_2(NITIm)_3]\cdot ClO_4$, $[Mn_2(NITBzIm)_3]ClO_4$ and $[Mn_2(NITIm)_3]BF_4$ ordered as weak ferromagnets at 1.4, 40 and 3.6 K, respectively, deserve special attention.[262]

The layered polymeric structure of these complexes with honeycomb motif is the same as that of the layered polymeric oxalate (see Fig. 1 *a*) or azide complexes (see Fig. 2). This fact agrees completely with the general requirement for the arrangement of a layered polymeric structure with a metal : bridging radical ratio of 3 : 2 with alternating chiral (Λ and Δ) fragments formed by the metal ions. This indicates that molecular ferromagnets of this structural type have a common architecture. A systematic study of magnetic-structural relationships only for compounds of this structural type will make it possible to obtain a series of molecular ferromagnets with different magnetic characteristics (critical temperatures, spontaneous magnetisation, coercive fields).

Like for oxalate molecular ferromagnets,[125, 263] the critical temperature of heterospin layered polymers was found to depend on the nature of uncoordinated anions (ClO_4^-, BF_4^-);[261, 262] varying the latter serves as an additional means for affecting the magnetic parameters of the solid phase. In addition, the interlayer distances in the imidazole complex $[Mn_2(NITIm)_3]ClO_4$ increase as the temperature is decreased, which decreases the critical temperature of this complex in comparison with the benzoimidazole complex $[Mn_2(NITBzIm)_3]ClO_4$.

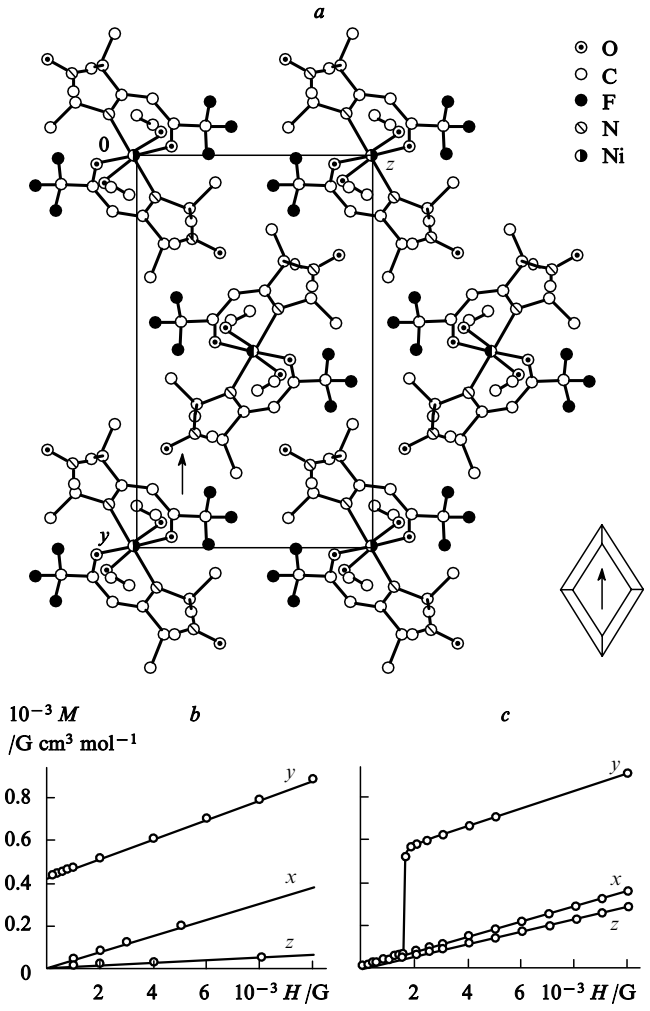
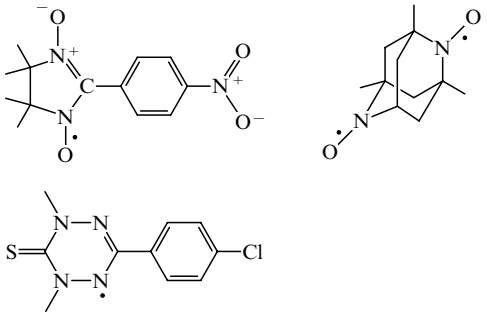


Figure 8. Scheme demonstrating the coincidence of the directions of the twofold symmetry axis (arrow inside the cell) and the direction of the easy magnetisation axis in the single crystal (arrow inside the crystal) for $NiL_2(EtOH)_2$ (*a*) and dependences of $\mu(H)$ showing the magnetisation anisotropy of single crystals of $NiL_2(MeOH)_2$ (*b*) and $NiL_2(EtOH)_2$ (*c*).[247]

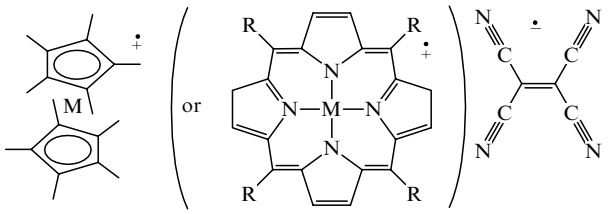
VI. The problem of organic ferromagnets

The general problem of the creation of molecular ferromagnets was intensely fed 15–20 years ago by theoretical studies[264–269] and experiments[270–275] aimed at the synthesis of the so-called high-temperature, purely organic ferromagnets, *i.e.*, compounds the solid phase of which has no metal-containing components at all. Experimental results on the synthesis of purely organic ferromagnets have not been confirmed in many aspects and are subject to criticism.[276–281] In the review[1] where the results of studies on organic ferromagnets were generalised and analysed in detail, it was noted that a most complex problem in the creation of such compounds is that the intermolecular exchange interactions in solid organic paramagnets are rather weak because of the large distances between the paramagnetic centres. In fact, the Curie temperatures for the purely organic ferromagnets known to date do not exceed 1–2 K.[282–303]



Perhaps, the only exception is the value of 16.1 K recorded for the adduct of C_{60} fullerene with tetrakis(dimethylamino)ethylene (TDAE) with composition $C_{60}(TDAE)_{0.86}$ (see Ref. 304). However, the nature of the ferromagnetism of $C_{60}(TDAE)_{0.86}$ remains unclear, although there was no doubt that the adduct did not contain ferromagnetic admixtures.

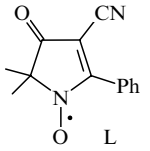
A series of molecular organometallic ferromagnets based on salts of sandwich radical cations of decamethylferrocenium type with radical anions of such π-acceptors as tetracyanoethylene or tetracyanoquinodimethane have been synthesised and studied.[3–6, 305–316]



The solid phases of these compounds involve molecular packing with alternating paramagnetic donors and acceptors (...$D^{+\bullet}A^{-\bullet}$...$D^{+\bullet}A^{-\bullet}$...). The reasons for the bulk magnetic ordering in them became the subject of extensive theoretical studies.[1, 6, 317–319] The compounds have critical temperatures from 2.3 to 8.8 K and are stable only in an inert atmosphere.

A similar series of donor-acceptor systems capable of magnetic ordering at 3–13 K was obtained from derivatives of porphyrin or phthalocyanine macrocyclic complexes with organic radical anions.[320–325] Judging by the temperature of bulk magnetic ordering, compounds of metals with the tetracyanoethylene radical anion (TCNE) with composition $M(TCNE)_2(CH_2Cl_2)_y$ [M = Mn^{II} (T_c = 75 K), Fe^{II} (T_c = 75 K)][326, 327] and especially the vanadium compound $V(TCNE)_x(CH_2Cl_2)_y$, where $x \simeq 2$ and $y \sim 0.5$, are prominent among these subjects. The latter compound behaves as a ferromagnet up to the temperature of thermal decomposition (> 350 K).[6, 328, 329] Unfortunately, the compound is extremely unstable in contact with air, and its structure could not be elucidated.

Nevertheless, it is substantiated that a phase which is saturated with an organic component and contains solvate molecules of dichloromethane (tetrahydrofuran or acetonitrile)[329] is capable of magnetic ordering at high temperatures. This means that, in principle, it is not forbidden to obtain purely organic ferromagnets with high critical temperatures in which the exchange interactions between the paramagnetic centres are sufficiently strong. Recently, we found in a study of the first stable vinylnitroxyl (L)[330]



that antiferromagnetic exchange chains with an exchange energy of $J/k \simeq 100$ K are formed in this solid. Due to such a high antiferromagnetic exchange energy, the magnetic moment of the radical L does not reach the theoretical value (1.73 μ_B) even at room temperature and equals 1.49 μ_B, *i.e.* high exchange interaction energies can also occur in compounds with a molecular structure. On the other hand, as already noted, mutual orientation of magnetic orbitals in the solid phase of L is such that the exchange interactions between the paramagnetic centres are antiferromagnetic, and the magnetic moment approaches zero as the temperature is lowered. However, examples of organic radicals are known in the solid phases of which the intermolecular exchange interactions are ferromagnetic[297, 298, 331–333] and even ferromagnetic chains are formed.[334] Besides, antiferromagnetic exchange is not an insurmountable obstacle to cooperative ordering, because a ferrimagnet can be obtained[267] by using heterospin bi- or polyradicals[335] or by cocrystallisation of mono- and bi- or polyradicals.[267] It is possible that a purely organic ferromagnet, maybe even one with a molecular structure and with a sufficiently high critical temperature (exceeding the boiling point of liquid helium) will be synthesised.

VII. Conclusion

This review analyses the main classes of chemical compounds for which the basic methods for designing high-dimensionality multispin systems which tend to cooperative magnetic ordering have been discussed. The development of any method for designing molecular ferromagnets is undoubtedly a laborious and lengthy process. About ten years ago, the determination of the first approaches to the design of various classes of molecular ferromagnets had only started. To date, vast and valuable experimental material has been accumulated: critical temperatures above room temperature (315–330 K) have already been achieved for molecular ferromagnets;[336, 337] compounds with anomalously high coercive fields have been synthesised;[180, 181] a number of compounds have been obtained as single crystals stable under ordinary conditions.[8, 247] The prospects of the practical application of molecular ferromagnets in various electronic and magnetic devices as well as for data recording, magnetic visualisation and protection against low-frequency magnetic fields are under discussion.[3, 6, 24] An original photomagnetic device with a cyanide molecular ferromagnet as a working element was shown at the XXXIIIrd International Conference on Coordination Chemistry.[35]

The prospects of progress in the area of molecular ferromagnets are difficult to predict. However, it is doubtless that these compounds are promising, as they represent light, transparent and mainly dielectric materials obtained under mild conditions, with specific properties commonly not typical of the classical magnetic materials.[338]

We did not dwell upon details of analysis of the magnetic properties of molecular ferromagnets, as this has been done exhaustively in several monographs,[13, 339–342] and a detailed discussion of the diversity of magnetic properties of molecular ferromagnets might be an independent topic of a separate review. Let us just note that the authors often introduce a large number of exchange parameters (J_1, J_2, J_3 *etc.*) in the spin-Hamiltonian when analysing the experimental temperature dependences $\chi(T)$ or $\mu(T)$ for complex multispin systems with various channels of exchange interactions. If this approach is used, it should be taken into account that the introduction of additional parameters improves the fitting of the experimental curves, but the errors of the model in the determination of the parameters can increase to such an extent (by several orders) that these additional parameters would be utterly uncertain.[343] The reliability of the exchange parameters obtained from the experiment is extremely important for the subsequent quantum-chemical analysis of the mechanisms of exchange interaction between the paramagnetic centres.

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