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# High Spin and Anisotropic Molecules Based on Polycyanometalate Chemistry

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**Summary.** This paper points out some recent achievements in the chemistry and physics of high spin and anisotropic molecules based on polycyanometalate complexes. Following a step by step synthetic strategy and using a localized electron orbital model, isotropic high spin molecules were obtained with ground spin states ranging from $S = 9/2$ to $27/2$. In the same way, anisotropic molecules with various nuclearities (bi, tri, tetra, hexa, and hepta-nuclear complexes) have been synthesized. Mixing these two approaches, it has been possible to obtained anisotropic high spin molecules that behave as single molecule magnets. The paper reviews some of the steps that lead to these findings and some of the prospects opened in the field of single molecule magnets.

**Keywords.** High spin molecules; Magnetic dendrimers; Molecular magnetism; Polycyanometalate chemistry; Photomagnetism; Single molecule magnet.

## 1. Introduction

In the field of molecular magnetism [1, 2], the search for new polynuclear molecules displaying high spin ground state raises the interest of synthetic chemists [3–8] and physicists [9–11] involved in nanomagnetism, because it provides new magnetic objects with specific and controlled characteristics. The properties of these complexes may be considered from both classical and quantum approach [12]. Possessing *a priori* well defined and uniform volume, shape, magnetic moment and anisotropy, these large spin molecules exhibit also original magnetism such as single molecule magnet behavior [13–18] (long relaxation time for the magnetization

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below a so-called blocking temperature, $T_B$) or magnetic quantum tunnelling effect [19, 20].

Our research approach has been always based on the synthesis of active molecules able to fulfill a particular function, such as molecular switches through the description of mixed valence species [21, 22], artificial enzymes based on porphyrins dimers and trimers [23, 24] or inorganic dendrimers acting as electrons reservoirs [25, 26]. In the same way, our present work is devoted to the synthesis of anisotropic high spin molecules in order to get single molecule magnets. It is briefly reviewed in the present paper.

## 2. Single Molecule Magnet

The investigation field is related to the so-called bottom-up approach of nanomagnetism: starting with mononuclear building blocks and reacting them together allows to get well characterized polynuclear complexes with high spins ground state and anisotropy. These species are of great interest to study the reversal of the magnetization in a magnetic field. The topic is both very fundamental (study of single-molecule magnets, evidence and study of the macroscopic quantum tunneling effect,...) and turned to applications (due to a possible enhancement of the information storage at the molecular scale).

The scheme in Fig. 1 allows to present simply the main physical parameters. First, in a polynuclear complex, the coupling between the spins $S_M$ and $S_{Mi}$ might be described by a phenomenological Hamiltonian,

$$\mathbf{H} = -J_{MM'}\left[\sum_{i,j} S_M(i) S_{M'}(j)\right] \tag{1}$$

leading to a spin state diagram. At low temperature, only the ground state is populated and the energy of the first excited state is proportional to the exchange

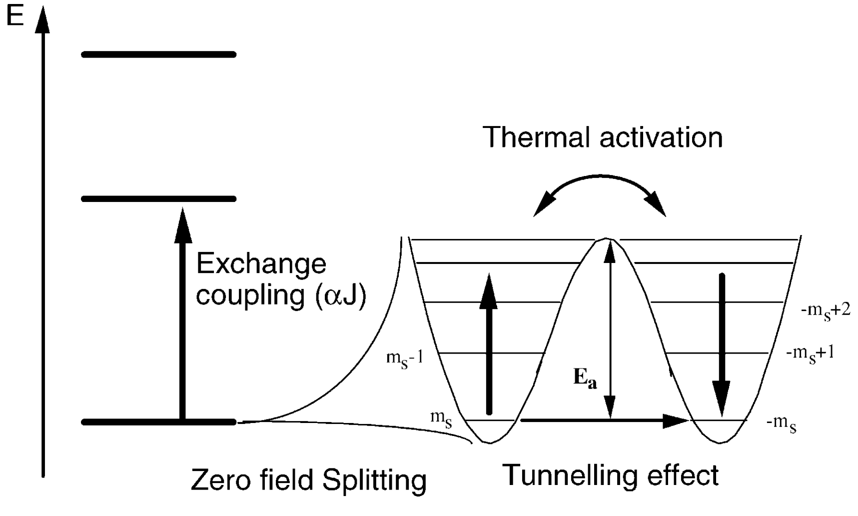


**Fig. 1.** Schematic plot of single molecule magnet experiencing axial zero field splitting

coupling, $J$. In presence of an uniaxial anisotropy, a zero-field splitting of the ground spin state is observed and the degeneracy of the ground state might be viewed as a two wells energy potential curve. The activation energy of the anisotropic barrier, $E_a$, between the spin states describing the two orientations of the magnetization, is a direct function of $D$ (uniaxial anisotropy) and $S$ (ground state spin value) following the equation $E_a = DS^2$ as indicated on Fig. 1.

To obtain a single molecule magnet, *i.e.*, to avoid the relaxation process, the spin as well as the absolute value of the anisotropy have to be as high as possible and $D$ has to be negative so that the state of highest $M_S$ lies below in energy. On the other hand, the exchange coupling, $J$, between two spin carriers has to be important to well separate the ground spin state from the excited states; the relative high value of the blocking temperature is dependent on it. Playing also an essential role, the intermolecular interaction, $J'_{inter}$, has to be negligible, necessary condition to avoid three-dimensional ordering and to observe the properties of an isolated nanoscale object. Very few examples of clusters responding to all these criteria have been described in the literature, among them $Mn_{12}$ [15, 16, 27], $Mn_4$ [11, 14], $Fe_8$ [10, 28] and more recently a series of molecules by Winnpenny [29] and Murrie [30].

Thus, in order to get a single molecule magnet, four parameters have to be taken into consideration in the design, the conception and the synthesis of the target molecules: the ground state spin value, $S$, the anisotropy, $D$, the exchange coupling, $J$, and the intermolecular magnetic interaction, $J'_{inter}$. Concerning the spin value, this is a matter of fact that, up to now, in most cases, serendipity has purchased nice and attractive high spin structures of great interest but without an effective control by the chemistry [8]. However, since our understanding increases, there exists undoubtedly a demand for more accurate design of clearly identified target molecules. As part of our research activities devoted to molecular magnetism, we are interested in synthesizing polynuclear compounds showing both large spin ground state value and anisotropy. In the present paper, the spin value, the anisotropy, the exchange coupling and the intermolecular interaction are discussed through the description of polynuclear complexes based on polycyanometalate precursors.

## 3. Rational Strategy to Obtain High Spin and Anisotropic Molecules

The synthetic strategy that has been initiated by *Mallah* in the laboratory [4, 31] and developed by ourselves [32–35] for the last few years, is based on a step by step modular approach. The key idea is the use of polycyanometalate precursors, as polyfunctional core and of specifically designed mononuclear complexes with only one accessible coordination site, the other sites being blocked by a polydentate chelate ligand. Thus, the reaction between theses two precursors, a *Lewis* base and acid, respectively, leads to polynuclear complexes with a radial symmetry (Fig. 2).

The main interest of such strategy is that the spin value is always high whatever the nature of the magnetic exchange interaction is (ferromagnetic or antiferromagnetic). Of further interest is the high solubility of the target species and their large charge, useful parameters to separate well the molecules from each other and then

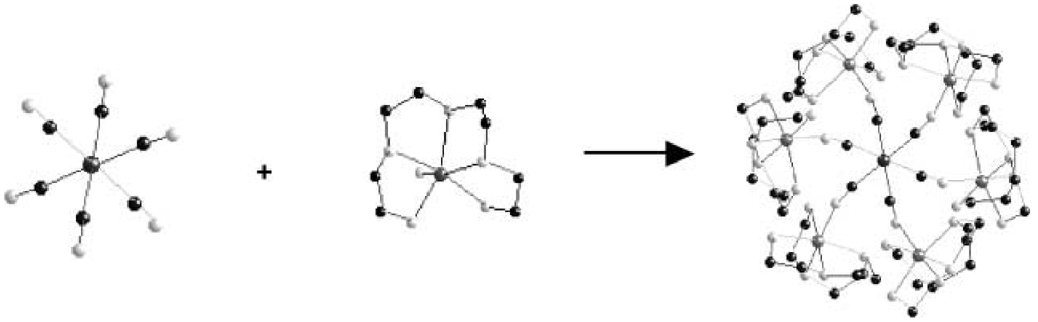


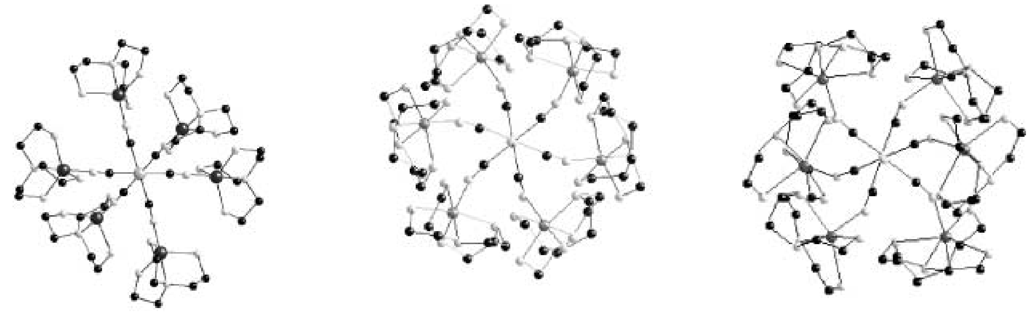
Fig. 2. Synthetic strategy

to minimize the intermolecular interactions. The other important point is the number of synthetic parameters to play with: the nature of the polycyanometalate cores, the polydentate ligand, the metallic ions, the stoichiometry, the counter anions, the solvent, etc ... Acting with these different criterions, it has been possible to synthesize a large amount of polynuclear complexes with various nuclearity, structural anisotropy and/or high spin value.

### *3.1. Control of the spin value [33]*

The nature of the metallic ions is the first parameter to modulate the spin value of the target polynuclear complex. Starting with an hexacyanochromate(III) complex and adding mononuclear species $[M(L)(H_2O)]^{2+}$ (with $L$ polydentate ligand, and $M = \mathrm{Cu^{II}}, \mathrm{Ni^{II}}, \mathrm{Mn^{II}}$), it has been possible to synthesize a series of heptanuclear complexes, $[\mathrm{Cr(CN{-}}M{-}L)_6]^{9+}$, ($L$ = *tren*, *tetren*, $M = \mathrm{Cu^{II}}, \mathrm{Ni^{II}}, \mathrm{Mn^{II}}$), noted $CrCu_6$, $CrNi_6$ and $CrMn_6$, characterized in solution by mass spectrometry and in solid state by X-ray crystallography on single crystal (Fig. 3).

The magnetic measurements have been performed on these three compounds, indicating the ferromagnetic nature of the interaction for $CrCu_6$ ($J = +45\,\mathrm{cm^{-1}}$) and $CrNi_6$ ($J = +17.3\,\mathrm{cm^{-1}}$) and the anti-ferromagnetic interaction for $CrMn_6$



**a) CrCu6 (S = 9/2)** **b) CrNi6 (S = 15/2)** **c) CrMn6 (S = 27/2)**

Fig. 3. Perspective view of three heptanuclear complexes: a) $CrCu_6$; b) $CrNi_6$; c) $CrMn_6$

($J = -9\,\mathrm{cm}^{-1}$). The first magnetization curves allow us to determine the ground state spin value for the three complexes and the experimental results are in good agreement with the expected value: $CrCu_6$ ($S = 9/2$), $CrNi_6$ ($S = 15/2$) and $CrMn_6$ ($S = 27/2$). A specific work is in progress in order to get heptanuclear complexes based on lanthanide ions and a particular attention is given to a potential $CrGd_6$ complex that might display a spin ground state equal to 45/2.

At low temperature ($T < 2$ K), despite the high spin values, the three compounds $CrCu_6$, $CrNi_6$ and $CrMn_6$, do not behave as single molecule magnet. This is well understood by the isotropy of these heptanuclear complexes and the absence of the anisotropic barrier $DS^2$.

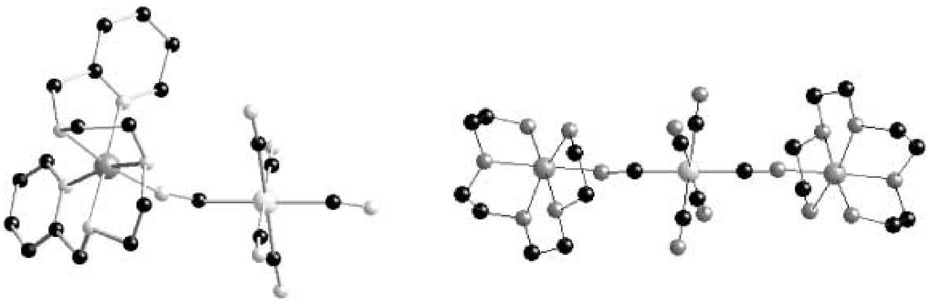
### *3.2. Control of the structural anisotropy [34, 35]*

The results obtained on the isotropic heptanuclear complexes indicate the necessity of introducing a structural anisotropy, as well as a high spin value. Changing the polydentate ligand and/or the counter anions, we succeeded in getting complexes of various nuclearity based on hexacyanometalate chemistry. Starting from hexacyanocobaltate(III), a thermodynamically stable diamagnetic center, and different Ni(II) mononuclear species, dinuclear (CoNi), *trans*-trinuclear ($CoNi_2$), *fac*-tetranuclear ($CoNi_3$), hexanuclear ($CoNi_5$) has been synthesized and characterized by X-ray crystallography (Fig. 4).

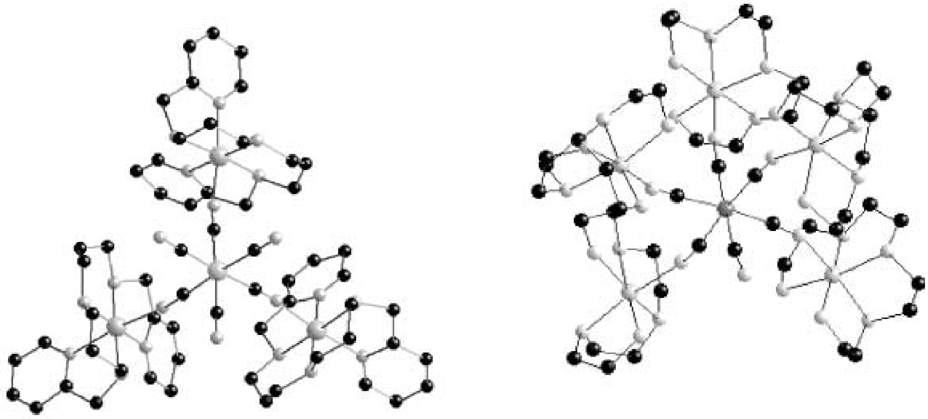
It appears that by using adapted ligands, it is possible to induce a specific nuclearity. Thus, with *dienpy2* and *dipropy2* ligands, trinuclear and tetranuclear complexes have been obtained selectively. The counter ions play also an important role in the formation of well defined polynuclear complexes. Thus, starting with *tetren* ligand in presence of nickel, chloride ions and hexacyanocobaltate(III), a trinuclear complex, $[Co(CN)_4(CN{-}Ni(\textit{tetren}))_2]Cl$, $CoNi_2$(*tetren*), appears to be the more thermodynamically stable product, instead of the hexanuclear species, $[Co(CN)(CN{-}Ni(\textit{tetren}))_5](ClO_4)_7$, $CoNi_5$, obtained in similar conditions but in presence of perchlorate ions. Similarly, the CoNi anion is formed when a large cation, *i.e.* tetraphenyl phosphate or tetraphenyl arseniate is introduced in the reaction medium. These results have been also observed with other transition metal ions, such as cobalt(II). All the polynuclear complexes obtained from hexacyanochromate(III) and hexacyanocobaltate(III) are summarized in Table 1.

Following a similar synthetic route $[Cr(CN)_5(CN{-}Ni(\textit{dienpy2}))](P(\textit{Phi})_4)$, CrNi ($S = 5/2$), $[Cr(CN)_4(CN{-}Ni(\textit{tetren}))_2]Cl$, $CrNi_2$(*tetren*) ($S = 7/2$) and $[Cr(CN)_4(CN{-}Ni(\textit{dienpy2}))_2](ClO_4)$, $CrNi_2$ (*dienpy2*) ($S = 7/2$) have been isolated as single crystals and characterized. Investigations on the magnetic properties of the CrNi and $CrNi_2$ complexes have been performed, indicating in all cases the ferromagnetic nature of the interaction between Cr(III) and Ni(II) through the cyanide ligand, as predicted by *Kahn*'s model based on the orthogonality of orbitals (*vide infra*). On the contrary, anti-ferromagnetic interactions are expected in case of orbital overlap.

The experimental data of the thermal dependence of $\chi_M T$ ($\chi_M$ being the magnetic susceptibilty) have been fitted by the *Van Vleck* equation, leading to the intramolecular exchange coupling constants. Concerning the dinuclear CrNi and the trinuclear compounds, $CrNi_2$(*tetren*) and $CrNi_2$(*dienpy2*), the resulting $J$ values



**a) CoNi** **b) CoNi2**



**c) CoNi3** **d) CoNi5**

**Fig. 4.** Perspective view of four polynuclear complexes with different geometry : a) CoNi; b) $CoNi_2$; c) $CoNi_3$; d) $CoNi_5$

are $+18$, $+10$ and $+5\,cm^{-1}$ respectively with an agreement factor of the order of $10^{-4}$. The result can be compared to the one obtained for $CrNi_6$ heptanuclear complex ($J = +17.3\,cm^{-1}$). The difference between the four coupling constants is due to the different values of the C–N–Ni angle (*vide infra*).

The magnetic measurements as well as EPR experiments allow us to determine the anisotropy constants, $D$, for all the polynuclear $CrNi_x$ complexes ($x = 1, 2, 6$). The first results indicate that, on one hand, heptanuclear complexes are isotropic high spin molecules ($D = 0\,cm^{-1}$), and on the other hand, dinuclear, CrNi and trinuclear $CrNi_2$ are anisotropic species ($|D| = 0.3\,cm^{-1}$) but with a modest spin value. Our intent is then to use the tools that have been developed in the previously described synthetic route to obtain simultaneously anisotropy and high spin value. Different strategies will be subsequently described.

### *3.3. Magneto-structural correlation [35]*

Seven different "$CrNi_x$" ($x = 1, 2, 6$) compounds have been isolated as single crystal and characterized including X-ray diffraction. The magnetic studies that

**Table 1.** Geometry, symmetry, spin ground state and interaction in polynuclear complexes synthesized from [$B$(III)(CN)$_6$] precursors [$B$(III) = Cr(III), Co(III)]

| Nuclearity | Complex | Geometry | Symmetry | Spin | Interaction[a] | $J$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| Bi | CrNi | | $D_{\infty h}$ | 5/2 | F | +18 |
| | CoNi | | $D_{\infty h}$ | 1 | | |
| Tri | CrNi$_2$-**A** | trans | $D_{\infty h}$ | 7/2 | F | +10 |
| | CrNi$_2$-**B** | trans | $D_{\infty h}$ | 7/2 | F | +10 |
| | CrNi$_2$-**C** | trans | $D_{\infty h}$ | 7/2 | F | +10 |
| | CrNi$_2$-**D** | trans | $D_{\infty h}$ | 7/2 | F | +5 |
| | CrNi$_2$-**E** | trans | $D_{\infty h}$ | 7/2 | F | +5 |
| | CoCo$_2$ | trans | $D_{\infty h}$ | 0 | af | ~0 |
| | CoCu$_2$ | cis | $C_2v/D_{\infty h}$ | 0 | af | ~0 |
| | CoNi$_2$-**A** | trans | $D_{\infty h}$ | 0 | af | ~0 |
| | CoNi$_2$-**B** | trans | $D_{\infty h}$ | 0 | af | ~0 |
| Tetra | CrNi$_3$ | facial | $C_{3v}$ | 9/2 | F | +18 |
| | CoCo$_3$ | Facial | $C_{3v}$ | frustration | af | ~0 |
| | CoNi$_3$ | Facial | $C_{3v}$ | frustration | af | ~0 |
| | CoCu$_3$ | mer | | 1/2 | af | ~0 |
| Hexa | CoNi$_5$ | | C4v | 1 | af | ~0 |
| Hepta | CrCu$_6$-**A** | octahedral | $O_h$ | 9/2 | F | +45 |
| | CrCu$_6$-**B** | octahedral | $O_h$ | 9/2 | F | +45 |
| | CrNi$_6$ | octahedral | $O_h$ | 15/2 | F | +17 |
| | CrMn$_6$ | octahedral | $O_h$ | 27/2 | AF | −9 |
| | CoCu$_6$-**A** | octahedral | $O_h$ | 0 | af | ~0 |
| | CoCu$_6$-**B** | octahedral | $O_h$ | 0 | af | ~0 |
| | CoMn$_6$ | octahedral | $O_h$ | 0 | af | ~0 |
| | CrNiMn$_5$ | octahedral | $O_h$ | 10 | F/AF | in progress |
| | CrNi2Mn$_4$ | octahedral | $O_h$ | 13/2 | F/AF | in progress |
| | CrNi2Ni$_4$ | octahedral | $O_h$ | 15/2 | F | in progress |

[a] F = ferro, AF = antiferro, af = weak antiferromagnetic interaction

have been performed on all species indicate in all cases a ferromagnetic interaction between the spin carriers as predicted by orbital models. The exchange coupling value, $J$, varies from $+4.5\,\mathrm{cm}^{-1}$ to $+18\,\mathrm{cm}^{-1}$ according to the nature of the product and more precisely as a function of the distortion of the cyanide bridge (the C–N–Ni angle).

Two models exist in order to foresee the $|J|$ value based on orbitals consideration: the *Hoffmann* (orthogonalized magnetic orbitals) and *Kahn* (non orthogonalized magnetic orbitals) models. Both predict that orthogonal orbitals give rise to ferromagnetism and that overlaps give rise to antiferromagnetism. One expression summarizes *Kahn*'s models in the case of two electrons 1 and 2 on two sites, described by two identical orbitals a and b. The singlet-triplet energy gap, $J$ ($J = E_S - E_T$) is given by Eq. (2):

$$J = 2k + 4\beta S \tag{2}$$

in which $k$ is the bielectronic exchange integral (positive) between the two non orthogonalized magnetic orbitals a and b; $\beta$ is the corresponding monoelectronic resonance (or transfer) integral (negative) and $S$ the monoelectronic overlap integral (positive) between a and b. When the two a and b orbitals are different, no rigorous analytical treatment is still available; a semi-empirical relation was proposed by *Kahn* [1, 36]:

$$J = 2k + 2S\ (\Delta^2 - \delta^2)^{1/2} \tag{3}$$

where $\delta$ is the initial energy gap between a and b orbitals, $\Delta$ is the energy gap between the molecular orbitals built from them.

In such approach, the exchange interaction, $J$, results from the addition of the two terms ($J = J_F + J_{AF}$), with a positive term, $J_F$, favoring a parallel alignment of the spins and ferromagnetism, and a negative term, $J_{AF}$, favoring an antiparallel alignment of the spins and short range antiferromagnetism.

In case of Cr(III) in an $O_h$ symmetry ($d^3$, $(t_{2g})^3$) and Ni(II) in an octahedral surrounding ($d^8$, $(e_g)^2$), the magnetic orbitals are orthogonal and ferromagnetic interaction is expected. Two different situations might be considered: (i) if the cyano bridge is close to linearity, the monoelectronic overlap integral is zero, $J = 2k$ and then the absolute value of the exchange coupling is maximum; (ii) on the other hand, the distortion of the cyano bridge induces a weak overlap of the orbitals ($S \neq 0$) leading to a $J$ value that corresponds to Eq. (3). In such a case the $|J|$ value decreases when the overlap increases.

The linear plot of the exchange coupling constant as function of the N–C–Ni angle (Fig. 5) allows to determine that the maximum $J$ value might be expected for strict orthogonality ($J_{max} = +35\,cm^{-1}$) and to predict that below 145 degrees an antiferromagnetic interaction will occur.

### 3.4. How to obtain anisotropic high spin molecules?

We have discussed previously the selective formation of isotropic high spin molecules through the description of $CrCu_6$ ($S = 9/2$), $CrNi_6$ ($S = 15/2$) and $CrMn_6$ ($S = 27/2$), as well as the synthesis of anisotropic complexes, such as CrNi ($S = 5/2$) and $CrNi_2$ ($S = 7/2$). Several synthetic strategies are presently developed in the laboratory in order to get anisotropic high spin molecules: (i) the synthesis of

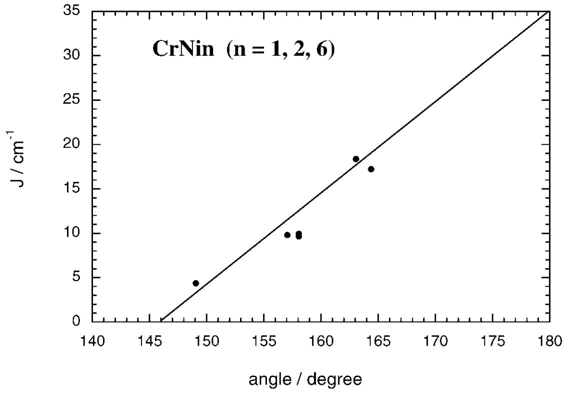


**Fig. 5.** Magneto structural correlation: $J = f(\theta)$

tetranuclear and hexanuclear complexes based on hexacyanochromate(III) chemistry, $CrNi_3$ and $CrNi_5$ for instance; (ii) the use of anisotropic metallic ions, such as Co(II) and Mn(III); (iii) the formation of heterotrimetallic complexes, *i.e.* $CrNi_2Mn_4$ and (iv) the use of anisotropic polycyanometalate cores.

### 3.4.1 Tetranuclear complex based on hexacyanochromate(III) chemistry [37]

The synthesis of the tetranuclear complex, $CrNi_3$, has been recently performed in the laboratory, starting from $[Ni(\mathit{dipropy2})(H_2O)]^{2+}$ isolated as crystalline perchlorate salt, in presence of the hexacyanochromate(III) precursor. No X-ray structure on single crystal has been solved but the other characterizations (infrared spectroscopy, mass spectrometry, elemental analysis and powder diffraction) and the similarities with the well defined $CoNi_3$ complex converge and confirm the nature of the product. The magnetic measurements on the $CrNi_3$ compounds indicate a ferromagnetic interaction between the spin carriers and corroborate the ground state spin value: $S = 9/2$. First AC measurements and the presence of an hysteresis loop at low temperature (30 mK) attest the presence of anisotropy in the compound that at first sight behave as a single molecule magnet. This result comforts us in our strategy to get, in a rational way, high spin and anisotropic molecules.

### 3.4.2 Polynuclear complexes based on anisotropic metallic ions [38]

We have seen previously the importance of the anisotropy to obtain a single molecule magnet. The structural anisotropy is the first important and necessary factor. The local anisotropy of the metallic ions is the second significant parameter. It has to be as high as possible: Mn(III), Co(II) and Ni(II) are good candidates for such an approach. The polynuclear complexes based on nickel(II) have been already synthesized and the preliminary results on $CrNi_3$ are in conformity with the expected single molecule magnet behavior. We planned then to build similar complexes based on Co(II) precursors. In presence of cobalt(II), we observed in most of the cases, during the synthesis, the hydrolysis of the hexacyanochromate(III) precursor and the formation of the thermodynamically stable $[Co(III)(CN)_6]^{3-}$. Then, the hexacyanocobaltate(III) reacts with the excess of the mononuclear cobalt(II) species present in solution inducing the formation of $CoCo_2$, $CoCo_3$ or $CoCo_6$ complexes depending on the synthetic conditions. Disappointing for the ‘‘single molecule magnets’’ approach, such compounds might be interesting from other points of view and specially the $CoCo_3$ complex that present an interesting *Landau-Zener* effect. Our observations point out the importance of the inertness of the molecular precursors in the success of our strategy: the bricks must be both stable and inert to control kinetic and entropic hindrances. So that, to obtain high spin and anisotropic molecules based on cobalt(II) peripheric metallic complexes, we are exploring new synthetic conditions. We are also dealing with promising Mn(III) derivatives.

### 3.4.3 Hetero-trimetallic complexes [39]

In order to get high spin and anisotropic complexes, we have recently developed a new synthetic strategy based on the formation of hetero-trimetallic complexes. The key idea is to use anistropic complexes such as CrNi or $CrNi_2$ as new precursors for the synthesis of polynuclear complexes. Thus, starting with $CrNi_2$ and adding a mononuclear Mn(II) complex to increase the spin value, it has been possible to isolate as single crystal a $CrNi_2Mn_4$ species that has been characterized by X-ray crystallography. The ligand *tetren* used for the nickel and the manganese is the same and no difference between the two metallic ions can be done on the crystallographic structure. Nevertheless, several evidences (cell parameters, mass spectrometry and X-ray fluorescence analysis) show unambiguously the formation of the expected compound. The magnetic studies performed on the compound indicate a high spin value for the ground state, $S = 13/2$. This result might be explained by a ferromagnetic interaction between Cr(III) and Ni(II) and antiferromagnetic interaction between Cr(III) and Mn(II), in agreement with the orbital model and the results obtained previously on $CrNi_6$ and $CrMn_6$. Preliminary results performed at low temperature indicate that, unfortunately, no significant improvement of the anisotropy and no single molecule magnet behaviors have been observed. The high symmetry of the heptanuclear complex and more especially the contribution of local anisotropy of the nickel ions explain this. Indeed, as shown previously, the total anisotropy of the polynuclear complex might be described by the sum of the local ($D_i$) and the coupling ($D_{ij}$) anisotropic factors associated to a specific coefficient following the equation:

$$D = \sum_i c_i D_i + \sum_{ij} c_{ij} D_{ij}$$

The calculation performed in collaboration with *Dante Gatteschi* indicates that, despite the high $D_{\mathrm{Ni}}$ value, the $c_{\mathrm{Ni}}$ parameter is very small and much lower than the $c_{\mathrm{Mn}}$ and $c_{\mathrm{Cr}}$ coefficients. It explains the small anisotropy of the whole polynuclear $CrNi_2Mn_4$ complex. Furthermore, it allows to determine the more promising anisotropic hetero di- or trimetallic compounds. Thus was built a $CrNi_2Ni_4$ complex (where the nickel(II) ions are surrounded with two different polydentate ligands) that behave as single molecule magnet and comfort us in the multi steps synthetic strategy.

### 3.4.4 Polynuclear complexes based on anisotropic cores [40, 41]

Most of the results described previously have been obtained with hexacyanometalate cores, such as $[Cr(CN)_6]^{3-}$ or $[Co(CN)_6]^{3-}$. We have discussed the limitation of these precursors, due to their octahedral symmetry, leading to isotropic heptanuclear complexes, with high spin value but no anisotropy. In the aim of building anisotropic high spin molecules, it is possible to use other polycyanometalate precursors, playing the role of *Lewis* base for the synthesis of polynuclear complexes with well-defined nuclearity. Starting with anisotropic cores, $[Cr(\mathit{acen})(CN)_2]^{+}$, $[Cr(Cp)(CN)_3]^{+}$, $[Cr(\mathit{phen})(CN)_4]^{-}$ or $[Cr(NO)(CN)_5]^{3-}$ for instance, and applying the synthetic strategy used successfully for the heptanuclear complex, it is planed to get selectively tri-, tetra-, penta- and hexa-nuclear complexes. The feasibility of such an approach has been demonstrated through the formation of $NiCu_4$ and $Fe(\mathit{phen})Cu_4$ complexes formed from $[Ni(CN)_4]^{2-}$ and $[Fe(\mathit{phen})(CN)_4]^{2-}$ starting materials and characterized by X-ray crystallography (Fig. 6) [40].

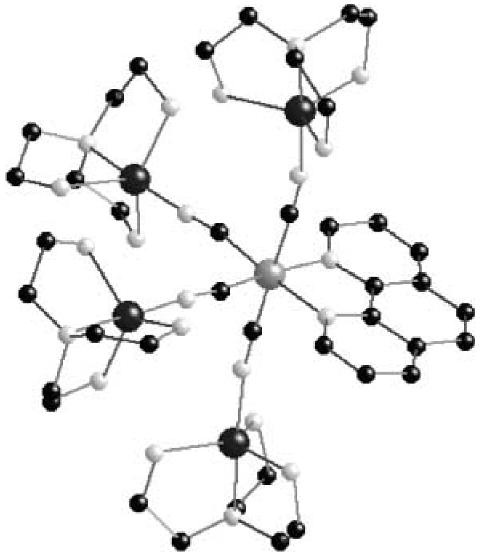


**Fig. 6.** Perspective view of a pentanuclear complex: Fe(phen)$Cu_4$

The octacyanometalate precursors might be viewed as an interesting family because of their anisotropic symmetry and the large number of accessible cyanide ligands. This might be of great interest for the spin value as well as the anisotropy. Furthermore, the more diffuse orbitals of these precursors might influence the exchange coupling value. The first attempts to obtain polynuclear complexes based on niobium(IV), molybdenium(V) and tungstate(V) complexes failed due to the hydrolysis of the niobium compounds and the reduction of the two other precursors. Nevertheless, heptanuclear complexes based on octacyanometalate chemistry, $[M(CN)_2(CN\text{–}M'(L))_6](ClO_4)_8$, ($M = W^{IV}$, $Mo^{IV}$, $M' = Cu^{II}$, $Ni^{II}$, and $Mn^{II}$), $WCu_6$, $WNi_6$, $WMn_6$, $MoCu_6$, $MoNi_6$ and $MoMn_6$, have been synthesized and fully characterized, including by X-ray crystallography. Assuredly, the compounds are made with a diamagnetic core and behave as six isolated paramagnetic species, but these compounds are of great interest for their photo-magnetic properties as discussed further [41].

## 4. New Achievements and Prospects

### 4.1. Supramolecular chemistry

The polynuclear complexes based on polycyanometalate chemistry that have been prepared and discussed previously might be used as new starting materials in the synthesis of more elaborate architectures. A large number of species with accessible cyanide ligands are now available, such as CrNi, $CrNi_2$, $CrNi_3$, $CoNi_5$, $MoCu_6$, etc... They are presently used in presence of an assembling mononuclear building block in order to get complexes of high nuclearity and higher spin value. The tools of supramolecular chemistry are widely used, such as the template effect or high dilution experimental conditions. Till now, these synthetic tools have been already used successfully including by ourselves [23] but they are not commonly employed in the molecular magnetic field. Following the routes opened by *Long* [42] very promising works are in progress.

### 4.2. Magnetic dendrimers

The chemistry of dendrimers, a novel field of research, is of real interest to build identical molecules (strictly monodisperse entities in the language of nanoscience) with a high number of branches. The flexibility of molecular chemistry allows not only to chose the chemical strategy (convergent or divergent) but also to design the branches so that the robust organic skeleton can complex metallic ions and catch at each generation a large and different number of metallic cations. However, very few examples of magnetic dendrimers are published in the literature and most of them are based on radicals [43]. It appears that the design of such architecture achieving at the same time (i) magnetic exchange interaction between the spin carriers, (ii) a high spin value of the ground state, and (iii) convincing characterization is a real challenge that we would like to take off. Our experience in the "dendrimer chemistry" [25, 26] and the molecular magnetism allows us to appreciate the difficulties of the approach, difficulties linked to the synthesis itself that has to involve quantitative yield reactions related to the construction of the skeleton and specific problems imposed by the magnetic requirements. Several synthetic strategies are nevertheless developed by our team in order to obtain magnetic dendrimers. Among them, we are dealing with i) design and synthesis of specific polydentate ligands, including radicals, ii) the design and the synthesis of organic dendrimers including specific coordination sites allowing exchange coupling between the spin bearers, and iii) design and synthesis of polynuclear complexes, their functionalization and a final assembling.

The polynuclear complexes $CrCu_6$ ($S = 9/2$), $CrNi_6$ ($S = 15/2$) and $CrMn_6$ ($S = 27/2$) described previously might be viewed as a first generation of magnetic dendrimers. Using the step by step synthetic strategy that has been developed in our laboratory and specific polydentate blocking ligand made with radicals, it might be possible to get multi-shell polynuclear complexes. In such architectures, the chromium plays the role of a polyfunctional core surrounded by the six metallic ions forming the first generation and the radicals are viewed as the peripheric shell, forming the second generation of spin carriers. The synthesis of compounds of that type has been done by *Rey* and *Verdaguer* allowing the formation of $[Fe_2Ni_3(\mathit{Rad})_6]$ viewed as a first example of high spin poly-shell complexes [44].

### 4.3. Photomagnetic high spin molecules

The molecular switch effect, extendedly used in molecular electronics, has always been part of our research activities, with the synthesis of designed species able to control the electron transfer. In molecular magnetism, the synthesis of photo-active materials are also present such as Co–Fe Prussian blue analogues [45–47], spin transition complexes or molecules presenting LIESST [48] or LDLIST [49] effect. But till now no one has succeeded to get a photo-active single molecule magnet. In our group, a very recent field of novelty is the design and the synthesis of photomagnetic high spin molecules. Our aim is then to modify the magnetic properties

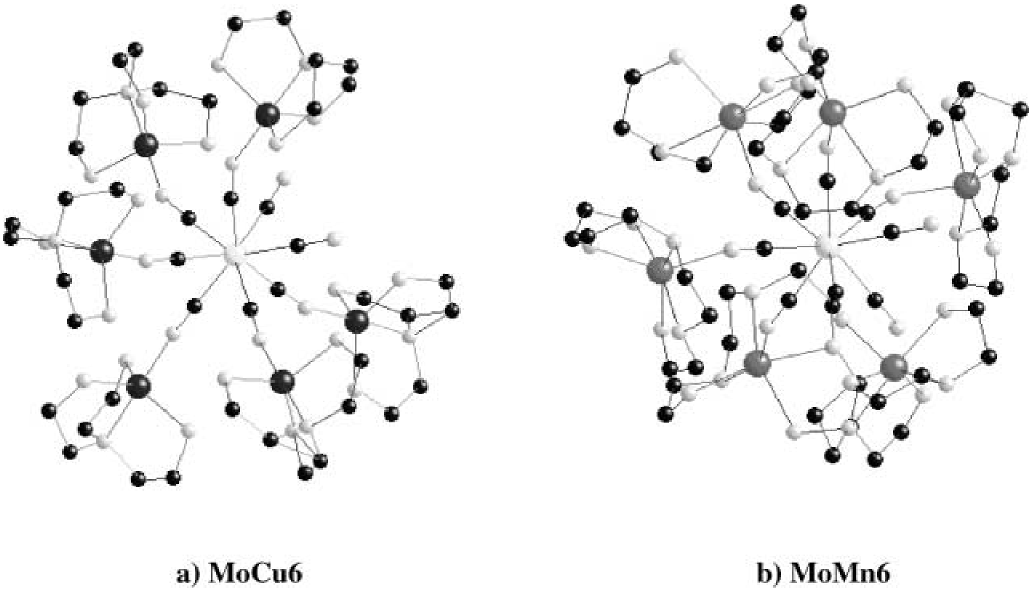


**Fig. 7.** Perspective view of two heptanuclear complexes: a) $MoCu_6$; b) $MoMn_6$

of the molecular entity using an external perturbation, such as a photonic irradiation. In continuation of the synthetic strategy herein described, we have selectively obtained heptanuclear complexes based on octacyanometalate diamagnetic precursors, Mo(IV) and W(IV). Then $MoCu_6$, $WCu_6$, $MoNi_6$, $WNi_6$, $MoMn_6$ and $WMn_6$ have been obtained and characterized by X-ray crystallography on single crystal and mass spectrometry (Fig. 7).

In collaboration with *C. Mathonière* (Bordeaux) who has previously suggested a possible electron transfer in MoCu Complexes [50], we have studied the photomagnetic properties of $MoCu_6$ complexes and demonstrated that before irradiation, the $Mo(IV)Cu_6$ complexes behave as six isolated paramagnetic centers, as expected by the presence of the diamagnetic center. After irradiation and a supposed electron transfer, the molecule behaves as a high spin molecule ($S = 3$) with ferromagnetic interaction between the spin carriers and the formation of paramagnetic centered species: $Mo(V)Cu(I)Cu(II)_5$. To our knowledge, the $MoCu_6$ appears as the first photomagnetic high spin molecule [41]. One has to consider that the phenomenon is reversible. Work is in progress (i) to evaluate the photomagnetic properties of the other complexes of the octacyanometalate family and (ii) in order to get not only photomagnetic high spin molecules, but also photomagnetic single molecule magnets.

## 5. Conclusion

We have developed a synthetic strategy and obtained selectively polynuclear complexes of high nuclearity and high spin value. A good understanding of the parameters involved in the single molecule magnet behavior permits us to design specific complexes and the step by step synthetic route allows us to get the tailor-made species with predicted and foreseen properties. The number of compounds obtained are of great interest for chemists to compare and to evaluate the best compounds to prepare, but also for physicists that have a complete family of products with interesting and diversified magnetic properties. The new fields of magnetic dendrimers or photomagnetic high spin molecules appear as promising areas of research for the future.

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