Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 453-462
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A Rational Route for Large Spin Molecules Based on Cyanometalate Complexes

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Polynuclear molecules with large-spin state and high anisotropy are discrete entities situated at the frontier between quantum and classical systems. These well defined complexes displaying uniform shape, magnetic moment and anisotropy can behave as single-molecule magnets. Following a bottom-up approach of nanomaterials, we present a rational synthetic route of such molecules based on hexacyanometalates $[M(CN)_6]^{3-}$cores. Thus, were built and fully characterised (mass spectroscopy, crystallographic structure, magnetic susceptibility, ...) polynuclear species such as $[M(CNM'L)_6]^{9+}$ or $[M(CN)_4(CNM'L)_2]^{+}$ (with M= Cr^{III}, Co^{III}, Fe^{III}; M'= Ni^{II}, Co^{II}, Cu^{II},... ; L =polydentate ligand) showing large ground spin states.

Keywords: large spin molecules; molecular magnetism; cyanometalate complexes

INTRODUCTION

The search for new polynuclear molecules displaying large spin ground state[1-5] raise the interest of synthetic chemists and nanomagnetism physicists because it provides new magnetic objects with specific characteristics. The properties of these complexes may be considered from both classical and quantum approach[6]. Possessing well defined and uniform volume, shape, magnetic moment and anisotropy, these large spin molecules exhibit also original magnetic behaviour such as superparamagnetism[7-8] (long relaxation time for the magnetisation below a so-called blocking temperature, T_B) or magnetic quantum tunnelling[9-12].

SYNTHETIC STRATEGY

In the bottom-up approach of nanomaterials, hexacyanometalates $[M(CN)_6]^{3-}$ are good precursors for the controlled synthesis of multinuclear molecules. The reaction of $[M(CN)_6]^{3-}$ as a Lewis base with mononuclear metal ions chelated by a multidentate terminal ligand, L (leaving one accessible coordination position only), leads to both trinuclear $[M(CN)_4(CNM'L)_2]^+$ and heptanuclear $[M(CNM'L)_6]^{9+}$ species (Fig. 1)

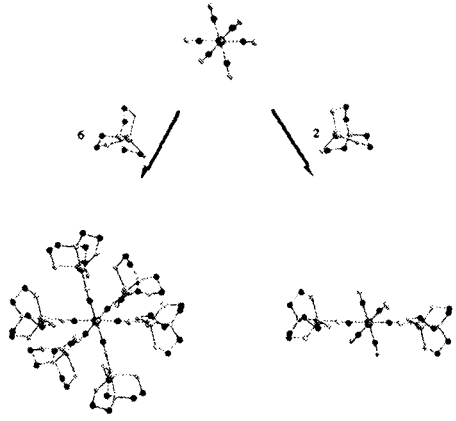
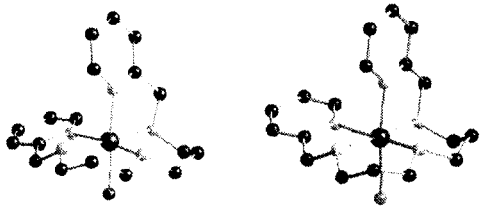


FIGURE 1 Synthetic strategy

Thus, in our laboratory, several examples of heptanuclear complexes have already been obtained and reported[13-14], namely $[Cr(CNNiL)_6]^{9+}$ and $[Cr(CNMnL)_6]^{9+}$ compounds exhibiting large spin ground state value of S= 15/2 and 27/2 respectively. Following this route, new tri- and heptanuclear species have been obtained, and are preliminary described in the present paper : $[Cr(CN)_4(CNNiL)_2]^+$ (with ClO_4^-, BF_4^- or Cl^- counteranions), $[Cr(CN)_4(CNCoL)_2](BF_4)$, and $[Cr(CNCuL)_6](ClO_4)_9$.

Most of these products have been synthesized by directly reacting the hexacyanochromate building block and the chosen mononuclear complex formed *in situ*.

In order to bypass the formation of side compounds induced by the "one pot" reactions, *vide infra*, a new synthetic strategy was sometimes required, the principle of which consists of first isolating and crystallizing the mononuclear complex before adding the hexacyanometalate core to the reaction mixture. Using this approach, we synthesized a series of specifically designed tetra- and penta-amine ligands, L, and their corresponding mononuclear complexes (M= Cu^{II}, Ni^{II}, Co^{II}) (Fig.2). In all cases, the tetra- or pentadentate ligands, L, allows the blocking of all the coordination sites except one which is occupied by a labile solvent molecule (water, methanol, ...) or a counteranion (Cl^-, ...), that can be easily substitued by the nitrogen atoms of the cyanide bridge.



$[Co(dipropy2)(H_2O)]^{2+}$ $[Ni\ (dipropy2)(Cl)]^{2+}$

FIGURE 2 Perspective view of two mononuclear cations

TRINUCLEAR COMPLEXES $[Cr(CN)_4(CNNiL)_2]^+$

Different trinuclear complexes $[Cr(CN)_4(CNNiL)_2]^+$ were obtained depending on the nature of the pentadentate ligands (L = tetraethylenepentamine (tetren), N,N''-bis(2-pyridylmethyl)diethylene-trisamine (dienpy2)) together with the counteranion (ClO_4^-, BF_4^-, Cl^-). In all cases, the mass spectroscopy (ES, Electrospray) gave satisfactory spectra with the molecular ions and confirmed the formation of the expected products. The trinuclear complexes in the solid were characterized by X-ray diffraction on single crystals and comparisons can then be made between the different structures. More specifically, the cristallographic data indicate a strong distorsion along the Cr-CN-Ni cyanide bridge with the Ni-N-C angle varying from 146 to 158 degrees (Fig. 3).

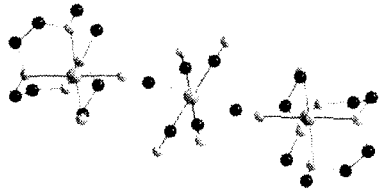


FIGURE 3 Perspective view of $[Cr(CN)_4(CNNi(tetren))_2]^+$ in **1**

The magnetic measurements have been performed on the different complexes and gave similar results. The thermal dependance of the molar susceptibility, $\chi_M T = f(T)$, performed on a Squid magnetometer, indicates that, upon cooling from 300 to 2K, $\chi_M T$ increases and no minimum is observed. On the other way, the magnetisation as a function of the applied field at 2K shows saturation value at 7 μ_B. These results demonstrate a short range ferromagnetic exchange interaction between Cr(III) and Ni(II) ions and the presence of low-lying spin ground state S = 7/2, as predicted by the localized electron orbital model (Fig. 4 and 5).

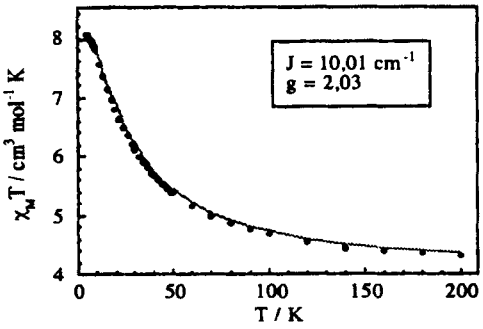


FIGURE 4 Thermal dependence of the molar susceptibility of **1** (• experiment; — best fit)

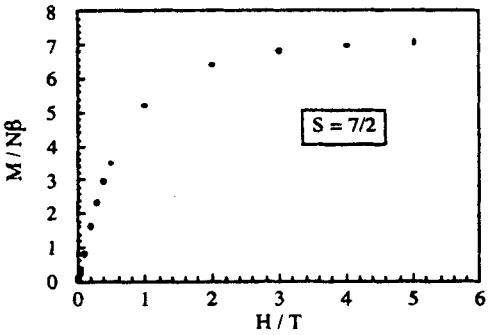


FIGURE 5 Magnetisation vs H for **1** at 2K

The experimental $\chi_M T = f(T)$ data were fitted to the analytical expression obtained from an Hamiltonian with isotropic interaction between Cr(III) and Ni(II) only. The resulting J values fluctuate around 10 cm^{-1} in different complexes (compared with $J = +16$ cm^{-1} in $[Cr(CNNiL)_6]^{9+}$ system[13]). The maximum ferromagnetic interaction is expected for 180° linear Cr-CN-Ni arrangement (strict orthogonality of the Cr(III) t_2g orbitals and the Ni(II) eg orbitals). The bending of the Cr-CN-Ni angle lowers the overall symmetry, introduces an overlap between the Cr(III) and the Ni(II) orbitals and creates

an antiferromagnetic contribution which lowers the absolute value of J. Calculations are in progress to correlate the Cr-CN-Ni angle to the experimental J value.

TRINUCLEAR COMPLEXES $[Cr(CN)_4(CNCoL)_2](BF_4)$

Despite the oxidation problems peculiar to the Co(II) chemistry, we succeeded in the synthesis and in the characterisation of the trinuclear complex $[Cr(CN)_4(CNCoL)_2](BF_4)$ (with L = dienpy2 = N,N''-bis(2-pyridylmethyl)diethylenetrisamine). The X-Ray diffraction analysis on single crystals shows a structure isomorphic to the one of the equivalent Ni(II) complex (Fig. 6).

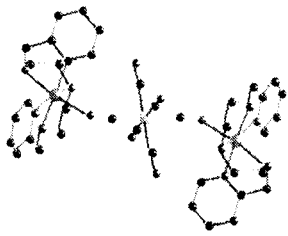


FIGURE 6 Perspective view of $[Cr(CN)_4(CNCoL)_2]^+$

Preliminary studies of the magnetisation and the thermal dependence of the molar susceptibility indicate (i) an antiferromagnetic interaction between Cr(III) and Co(II), leading to a molecular spin ground state S = 3/2; and (ii) an important role of the Co(II). The antiferromagnetic interaction is clearly related to the overlap of the Cr(III) t_2g and Co(II) t_2g orbitals and to the decrease of the ferromagnetic contribution Cr(III) t_2g -Co(II) eg due to the strong bending of the bridge (C-N-Ni angle =142.9°). It will be necessary to take into account the Co(II) orbital moment in the magnetic properties.

HEPTANUCLEAR COMPLEX $[Cr(CNCu(tren))_6]^{9+}$

The polynuclear complex $[Cr(CNCutren)_6]^{9+}$, was obtained by a dropwise addition of a tripotassium hexacyanochromate solution to a water/acetonitrile solution of the mononuclear copper(II) complex generated *in situ* from a commercially available ligand, tris(2-aminoethyl)amine (tren), and Cu(II) perchlorate salt. The product was unambiguously identified in solution by mass spectroscopy (ES, Electrospay): the spectra shows a peak at m/z = 1080 which is assigned to (molecular peak - $2ClO_4)^{2+}$. The X-ray diffraction structure of the corresponding blue crystals, indicates the presence of the expected heptanuclear compound. The crystal structure displays also two "parasitical" trinuclear complexes $[tren(Cu(tren))_3]^{6+}$ (Fig. 7). The trinuclear copper(II) species can be synthesized alone by another route and isolated. Up to now, it is not the case for the heptanuclear one[15].

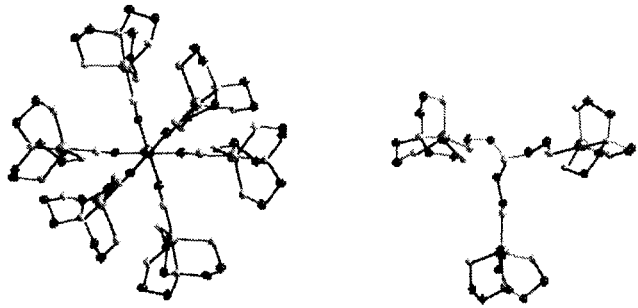


FIGURE 7 Perspective view of $[Cr(CNCutren)_6]^{9+}$ and $[tren(Cu(tren))_3]^{6+}$ cations

The magnetic susceptibility of the complex $[Cr(CNCu)_6]^{9+}$, measured in **2** with a SQUID magnetometer in the temperature range of 2-300K and the magnetisation in the 0-5 T magnetic field domain, corrected for the paramagnetic contribution of the trinuclear complex, $[tren(Cu(tren))_3]^{6+}$, demonstrate a ferromagnetic interaction between the Cr(III) and the Ni(II) ions. The ferromagnetic interaction is in perfect agreement with the orthogonality of the Cr(III) t_2g and the Cu(II) eg orbitals. The $\chi_M T$ thermal

dependence of the corrected $\chi_M T$ clearly shows that upon cooling, $\chi_M T$ increases continuously from room temperature and does not exhibit any minimum (Fig. 8). The $\chi_M T$ experimental data were successfully fitted to the analytic expression using the adequate spin hamiltonian where the interaction between the Cu(II) cations and the zero field splitting are assumed to be negligible (Fig. 8, 9).

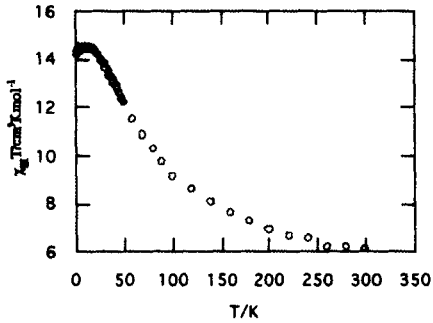


FIGURE 8 Thermal dependence of the molar corrected susceptibility in **2**

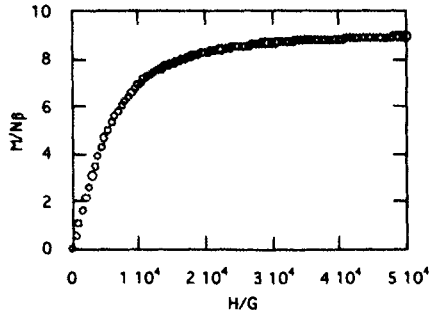


FIGURE 9 Corrected magnetisation vs H of $[Cr(CNCu)_6]^{9+}$ in **2**

The corrected magnetisation measurement as a function of the applied field shows a saturation value at 9 μB and demonstrate a large spin ground state value, S = 9/2.

We synthesized as well trinuclear and heptanuclear complexes with a diamagnetic ion at the center (Co^{III}, Fe^{II}, ...) and we are working on other paramagnetic cores (Fe^{III}, Mn^{III}, transition metal ions of the 2nd and 3rd rows, ...) and peripheral transtion metals (lanthanides, ...). We also obtained as by-products μ-cyano homo dinuclear complexes not reported here, since they correspond to strongly antiferromagnetically coupled complexes with singlet ground states. We assigned their formation to the lability of some hexacyanometalates ($[Fe^{III}(CN)_6]^{3-}$, $[Mn^{III}(CN)_6]^{3-}$, ...).

CONCLUSION

Owing to the nature of the cyanide ligand, it is possible to predict and to tune the orbital interactions, the ground state spin value of the molecules, choosing the nature and the number of metallic centers involved.

To synthesize molecules not only with high-spin ground state but also a tunable anisotropy, we are currently (i) carrying out further studies in order to change central and peripheral transition metals and to synthesize lower symmetrical complexes, i.e. tetra, penta and hexanuclear compounds of the same family; (ii) trying to better understand how the ground state anisotropy arises from the local ion anisotropies in a given symetry [16].

We focus in this contribution on the possibility to tune the ground state spin value from 3/2 to 27/2 by controlling the overlap between the magnetic orbitals in the polynuclear complexes. To get systems with a ground state populated at room temperature enhanced J values between the paramagnetic cations are needed ($|J| > 300$ K).

The search for single molecule magnets or new examples of quantum tunneling of the magnetisation necessitates the control not only of the spin value of the ground state, but also of its anisotropy since the anisotropy

barrier, in a uniaxial system is $\Delta = DS_z^2$. A room temperature single molecule magnet would necessitate $\Delta > 400$ K, i.e., for example S = 20 and D = 1K). On the contrary quantum tunelling of the magnetisation would imply lower D values.

Ackowlegment

We thank Florence Gonet, University Pierre et Marie Curie in Paris, for the Mass Spectroscopy studies and European Community for financial support (TMR n° FMRXCT980181)

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