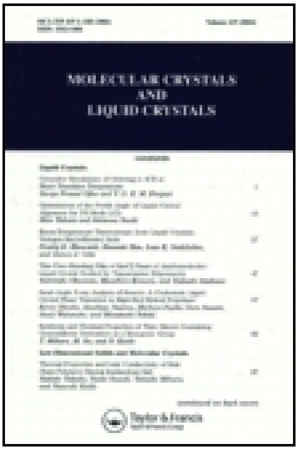

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Cyanide-Bridged Bimetallic High Spin Molecules

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To cite this article: Arnaud Marvilliers, Talal Mallaha, Eric Rivierea, Simon Parsons, Carmen Munozc & Kira E. Vostrikovad (1999): Cyanide-Bridged Bimetallic High Spin Molecules, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 483-494

To link to this article: http://dx.doi.org/10.1080/10587259908028890

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 483-494
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Cyanide-Bridged Bimetallic High Spin Molecules

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The synthesis, characterisation and magnetic properties of two series of polynuclear cyanide-bridged high spin molecules are presented. Tetranuclear compounds of general formula $(NC)_3M(CNM'L_5)_3{\bullet}7H_2O$ ($M = Fe^{III}, Cr^{III}$ and $M' = Mn^{III}, Fe^{III}$) are obtained by using peripheral complexes with pentadentate ligands. Pentanuclear complexes $((NC)_3Cr[CNNi(ligand)_2NC]_3Cr(CN)_3{\bullet}6H_2O)$ are designed owing to steric hindrance induced by bulky bidentate ligands chelating the peripheral Ni^{II} complexes. The magnetic properties show that ground states with spin up to 9 may be obtained.

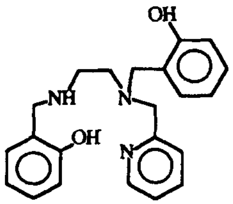
Keywords: high spin molecules; metallocyanide; cyanide-bridged; iron(III); manganese(III); chromium(III); magnetism

INTRODUCTION

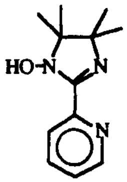
The last decade has seen the emergence of a new kind of polynuclear complexes. These molecules may contain a large number of interacting paramagnetic metal ions leading to a high spin ground state[1-3]. When magnetic anisotropy is present, a nanomagnet behaviour may be observed at low temperature[4-7]. For the first time, macroscopic tunnelling of the magnetisation was evidenced in 1996 in Mn_{12}[8,9].

In most cases, a "one pot" reaction leads through a self-assembling process to high spin molecular clusters. An alternative strategy consists of building around a central core "step by step" such molecules. Using hexacyanochromate(III) as a central paramagnetic "complex as ligand" we were able to synthesise in a two steps reaction heptanuclear complexes with spin ground states up to 27/2[10-12]. One of these molecules[10] of formula $[Cr(CNNi(tetren))_6](ClO_4)_9$ was the first cluster of half integer spin ground state (S = 15/2) to show the tunnelling of the magnetisation at low temperature[13]. Two other examples of clusters with half integer spin ground states (S = 9/2 and 19/2) were recently reported[14,15].

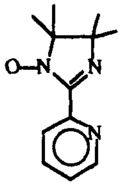
In our continuing program aiming at the design of high spin molecules, we report here the synthesis and the magnetic properties of two series of compounds. Series 1 consists of tetranuclear complexes of general formula $(NC)_3M(CNM'L_5)_3 \cdot 7H_2O$ where M is Cr^{III} or Fe^{III} and M' is Mn^{III} or Fe^{III} ; L_5 is a pentadentate ligand. Its protonated form H_2L_5 is represented in scheme 1. Series 2 consists of two pentanuclear complexes of formula $(NC)_3Cr[CNNi(ligand)_2NC]_3Cr(CN)_3 \cdot 6H_2O$. The two compounds differ by the nature of the Ni^{II} ligand. The two ligands noted L_2 and R_2 are shown in schemes 2 and 3 respectively. L_2 is bidentate and diamagnetic while R_2 is the pyridine-iminonitronyl radical.



scheme 1



scheme 2



scheme 3

SYNTHESIS AND CHARACTERISATION

H_2L_5

H_2L_5 is obtained by a three steps reaction from the Schiff base H_2salen. The first step consists of reducing H_2salen by $NaBH_4$ in methanol. The reaction of the reduced H_2salen with 2-pyridine carboxaldehyde leads to the aminal derivative. The third step is the reduction of the aminal derivative by $NaBH_3CN$ in methanol.

$[M'L_5Cl]$ $(M' = Fe^{III}$ and $Mn^{III})$

To an ethanolic solution of H_2L_5 is added two equimolar amounts of triethylamine. The resulting solution is added dropwise to the metal salt ($Fe^{III}Cl_3 \cdot 6H_2O$ or $Mn^{II}Cl_2.xH_2O$) dissolved in ethanol.

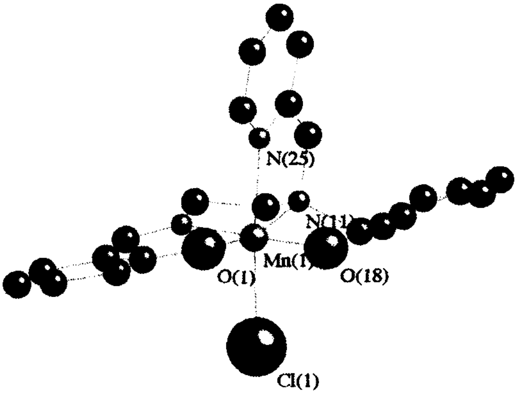


FIGURE 1 Representation of the structure of $[MnL_5Cl]$. Selected distances are : Mn-O(18) = 1.856(8) Å, Mn-O(1) = 1.893(9) Å, Mn-N(8) = 1.980(10) Å, Mn-N(11) = 2.124(11) Å, Mn-N(25) = 2.264(12) Å and Mn-Cl = 2.576(4) Å.

After heating gently for about 15 minutes a precipitate appears. Elemental analysis fits well the proposed formula. The structure of $[MnL_5Cl]$ was determined on single crystals obtained by slow evaporation of a methanolic solution. The compound crystallises in the Pbca space group of the orthorhombic system. The surrounding of the metal ion is highly distorted as shown by the metal-ligand distances (Fig. 1).

$[(NC)_3M(CNM'L_5)_3]{\cdot}7H_2O$ $(M= Cr^{III}, Fe^{III}$ and $M' = Fe^{III}, Mn^{III})$

The tetranuclear complexes precipitate in water when two solution containing the stoichiometric amounts of $K_3[M(CN)_6]$ and $[M'L_5Cl]$ are mixed together.

The order of mixing the two solutions has no influence on the M'/M metal ions ratio. Infra-red spectra show clearly the presence of bridging and non-bridging cyanides, and elemental analysis fits well the proposed formula. The structure of the tetranuclear complexes has not been solved because the lack of suitable single crystals for all compounds. However, due to the presence of only one potentially substitutable ligand (Cl) in the co-ordination sphere of M' only molecular species and not extended systems are expected. Two different spatial arrangements of the peripheral complexes around the hexacyanometallates are possible : facial and meridional.

[Ni(ligand)$_2$NO$_3$]NO$_3$

A solution of Ni(NO$_3$)$_2$·6H$_2$O in acetonitrile is added dropwise to a solution of L$_2$ (or R$_2$)[16] in the same solvent. A precipitate is obtained on evaporating the solution to 1/2 of its volume. The two compounds were characterised by infra-red spectroscopy and elemental analysis.

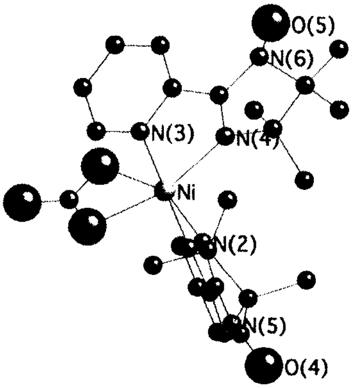
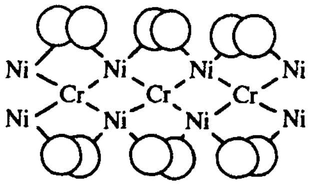


FIGURE 2 Representation of the structure of [Ni(L$_2$)$_2$NO$_3$]NO$_3$.

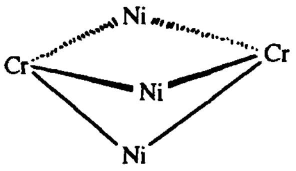
When the mother solution of [Ni(L$_2$)$_2$NO$_3$]NO$_3$ is left in the dark, single crystals appear within 24 hours and were used to solve the structure (Fig. 2). The surrounding of the metal is octahedral. It consists of two L$_2$ bidentate ligands in a cis arrangement and one nitrate anion occupying the two remaining positions. It is worth noting that the L_2 ligand is chelating the nickel atom by its two nitrogen atoms. No suitable single crystals were obtained for $[Ni(R_2)_2NO_3]NO_3$.

$(NC)_3Cr[CNNi(ligand)_2NC]_3Cr(CN)_3 \cdot 6H_2O$

The two compounds precipitate in water when mixing two solutions containing the stoichiometric amounts of $K_3[Cr(CN)_6]$ and $[Ni(ligand)_2NO_3]NO_3$. The infra-red spectra show clearly the presence of two bands at 2170 and 2130 cm^{-1} assigned to bridging and non-bridging cyanides respectively. Unfortunately, it was not possible to grow suitable single crystals for structural studies. The important characteristics of the two compounds is their solubility without decomposition in different solvents like methanol, ethanol and acetonitrile while being insoluble in water. This is a good hint for their molecular nature. In order to understand the spatial arrangement of the five (2 Cr^{III} and 3 Ni^{II}) metal ions we used CPK molecular models. The important feature we discovered is the presence of steric hindrance between two nickel complexes bridged by a $Cr(CN)_6$ molecule as shown in scheme 4. This precludes the formation of an extended system and should lead to a tetranuclear $[Cr_2Ni_2]^{2-}$ complex leaving four non-bridging cyanide groups on each chromium atom. However, elemental analysis shows clearly that the Ni/Cr ratio is 1.5.



scheme 4



scheme 5

The molecular model shows that putting a third nickel complex bridging the two chromicyanide molecules does not lead to any steric hindrance ; the three nickel complexes are then at the vertices of an equilateral triangle as shown in scheme 5.

MAGNETIC PROPERTIES : RESULTS AND DISCUSSION

$[(NC)_3Cr(CNM'L_5)_3]\cdot 7H_2O.$

For $CrFe_3$, the $\chi_M T$ value at room temperature (14.60 cm^3 K mol^{-1}) is slightly less than what is expected for isolated ions (15 cm^3 K mol^{-1} for g = 2). When the temperature is lowered $\chi_M T$ decreases, reaches a minimum at T = 14 K, increases slightly and then decreases below T = 5 K (Fig. 4).

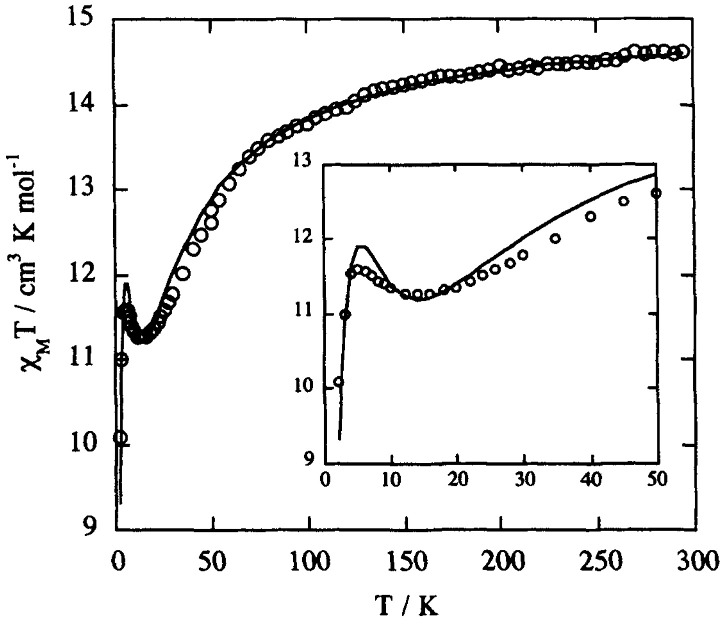


FIGURE 4 $\chi_M T = f(T)$ experimental (o) and calculated (-) data for $CrFe_3$.

Our first attempt was to fit the data using the following hamiltonian :

$$H = -J_{MM'} S_M \left(S_{M'_1} + S_{M'_2} + S_{M'_3} \right) - J_{M'M'} \left(S_{M'_1} S_{M'_2} + S_{M'_1} S_{M'_2} + S_{M'_1} S_{M'_2} \right) + g\beta H S_z \qquad (1)$$

where $J_{MM'}$ is the exchange coupling parameter between the central and the peripheral metal centres and $J_{M'M'}$ between the peripheral centres. No good fit could be found mainly because the decrease of $\chi_M T$ below 5 K that could not be modelled with reasonable values of $J_{MM'}$ and $J_{M'M'}$. The presence of water molecules (7 for each tetranuclear complex) led to the assumption of the presence of intermolecular interactions at low temperature. Using the modified hamiltonian of eq. 2 :

$$H = - J_{MM'} S_M \left(S_{M_1'} + S_{M_2'} + S_{M_3'} \right) + g\beta H S_z - zj\langle S_z \rangle S_z \quad (2)$$

where the last term describes the intermolecular interaction in the molecular-field approximation[17], it was possible to obtain a good fit of the experimental data with J_{CrFe} = - 2.27 cm^{-1}, g = 2.00 and zj = - 0.12 cm^{-1} (R = 1.2 10^{-4}, see Fig. 4). It is worth noting that preliminary thermogravimetric analysis (TGA) shows that *only part* of the seven water molecules can be removed (under vacuum at T = 370 K) before decomposition occurs. This is in favour of the presence of a hydrogen bond network linking the molecular species together responsible of intermolecular interactions.

For $CrMn_3$ the behaviour is similar to that of $CrFe_3$. At T = 300 K, $\chi_M T$ (10.46 cm^3 K mol^{-1}) corresponds to that of isolated ions (10.69 cm^3 K mol^{-1} for g = 1.98). The main difference is the absence of neat minimum and maximum at low temperature. Fitting the experimental data (Fig. 5) to the susceptibility expression derived from the hamiltonian of eq. 2 leads to J_{CrMn} = - 2.14 cm^{-1}, g = 1.98 and zj = - 0.19 cm^{-1} (R = 6.2 10^{-5}). The higher value of zj for $CrMn_3$ expresses a stronger intermolecular interaction within this compound. This can be correlated to the absence of a minimum in the $\chi_M T$ curve.

Even though the molecular species possess a high spin ground state (S = 6 and 9/2 for $CrFe_3$ and $CrMn_3$ respectively), the intermolecular interactions at low temperature lead to lower spin values in the solid state. In order to reveal the properties of single molecules, susceptibility and magnetisation measurements in solution are underway. This should confirm the nature of the ground state for the tetranuclear species.

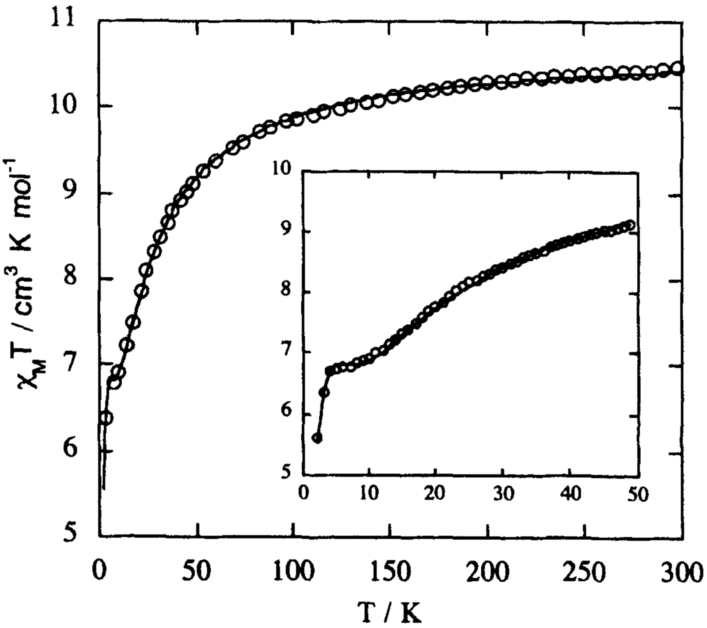


FIGURE 5 $\chi_M T$ = f(T) experimental (o) and calculated (-) data for $CrMn_3$.

$[(NC)_3Fe(CNM'L_5)_3]\cdot 7H_2O$

Substituting $Cr(CN)_6^{3-}$ by $Fe(CN)_6^{3-}$ leads to similar compounds noted $FeFe_3$ and $FeMn_3$. Although there is no alteration in the chemical behaviour, the magnetic properties change dramatically (Fig. 6). When the temperature is lowered $\chi_M T$ increases indicating a ferromagnetic exchange coupling between the central Fe^{III} and the peripheral Fe^{III} and Mn^{III} ions. Fitting the data with the hamiltonian of eq. 2 gives J values of + 6 and + 10 cm^{-1} for $FeFe_3$ and $FeMn_3$ leading to a spin ground state of 8 and 13/2 respectively. The nature of the exchange interaction changes from antiferromagnetic to ferromagnetic when Cr^{III} is substituted by Fe^{III}. For CrM'_3 the overall antiferromagnetic exchange interaction is weak which means that the balance between the ferro- and the antiferromagnetic contributions to the interaction is almost equal. Small electronic and/or structural difference from one compound to another may induce a slight change in the amplitude of each exchange contribution. Floriani *et al* has reported two systems containing the Fe^{III}-CN-Mn^{III} sequence, one extended[18] and the other molecular[19]. The exchange interaction has been found to be ferromagnetic in the former and antiferromagnetic in the latter.

As for the chromium based compounds, antiferromagnetic intermolecular interaction is operative at low temperature.

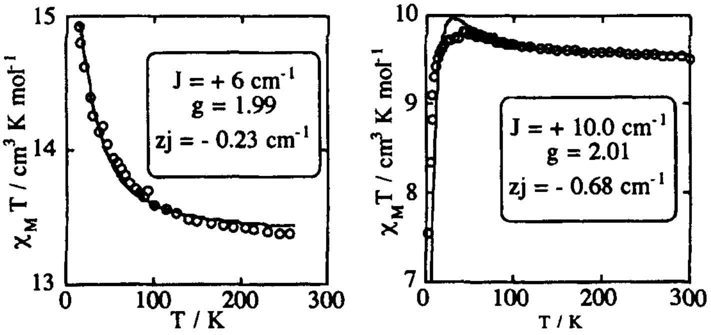


FIGURE 6 $\chi_M T$ = f(T) experimental (o) and calculated (-) data for $FeFe_3$ (left), and $FeMn_3$ (rignt).

$[Ni(ligand)_2NO_3]NO_3$

When "ligand" is L_2 (scheme 2), a Curie law is observed between room temperature and T = 50 K. The decrease below 50 K indicates the presence of zero-field splitting within the S = 1 state. Fitting the magnetic data leads to g = 2.18 and D = 6.14 cm^{-1}.

When ligand is R_2 (scheme 3), the $\chi_M T$ value (fig. 7) at T = 300 K (2.45 cm^3 K mol^{-1}) is higher than what is expected for isolated one Ni^{II} (S= 1) and two radicals (S = 1/2) (1.94 cm^3 K mol^{-1} for g_{Ni} = 2.18). On lowering the temperature, $\chi_M T$ increases first and reaches a value of 2.734 cm^3 K mol^{-1} at 90 K then slowly decreases at lower temperature. The behaviour at high temperature is consistent with a ferromagnetic interaction between Ni^{II} and the two radicals leading to a S = 2 ground state. The decrease at low temperature may be the result of mainly two effects: zero-field splitting and/or intermolecular antiferromagnetic interaction mediated by the radicals N-O groups. The best fit (considering intermolecular interactions) leads to $J_{Ni\text{-}R2}$ = + 207 cm^{-1}, g = 1.99 and zj = -1.9 cm^{-1}.

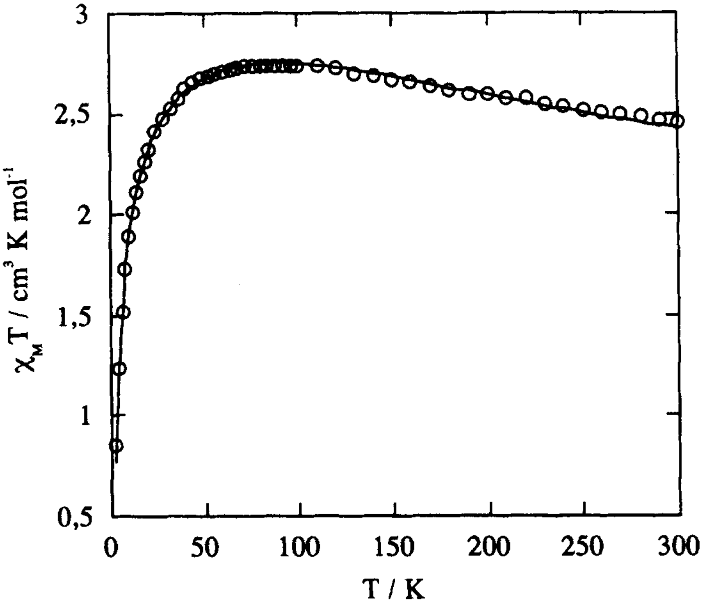
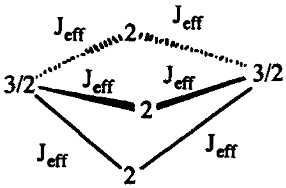


FIGURE 7 $\chi_M T$ = f(T) experimental (o) and calculated (-) data for $[Ni(R_2)_2NO_3]NO_3$

$(NC)_3Cr[CNNi(ligand)_2NC]_3Cr(CN)_3{\cdot}6H_2O$

The behaviour of $\chi_M T$ between 300 and 50 K for "ligand" = L_2 indicates a ferromagnetic interaction ; this is expected between Cr^{III} and Ni^{II} bridged by cyanide[10]. Below T = 50 K, $\chi_M T$ increases more than what is expected for mere intramolecular interaction indicating the presence of intermolecular ferromagnetic coupling (fig. 8, left). This leads to the occurrence of a ferromagnetic order at T = 5 K confirmed by the presence of remnant magnetisation at $T = 2$ K (not presented here). Since no crystal structure is available, it is difficult to track the origin of the magnetic order at low temperature. Magnetic measurements in solution will soon be carried out.

When "ligand" is R_2 an overall ferromagnetic interaction is observed as expected. No ordering occurs at low temperature in this case. Fitting the data is not possible using the Kambé model. But since we know that J_{NiR2} (207 cm^{-1}) is much stronger than J_{CrNi} (15 cm^{-1})[10], we have assumed that below 150 K only the ground state $S = 2$ of the $Ni(R_2)_2$ fragments has an important contribution to the magnetic susceptibility. This led us to consider only the interaction between the two Cr^{III} ($S = 3/2$) states and the $S = 2$ ground states of the three $Ni(R_2)_2$ fragments as shown in scheme 6 ; the exchange parameter is noted J_{eff}. Using the spin projection of the local spins ($S_{Ni} = 1$, $S_{R2} = 1/2$) on the $S = 2$ total spin, it is possible to show that J_{eff} is equal to $J_{CrNi}/2$.



scheme 6

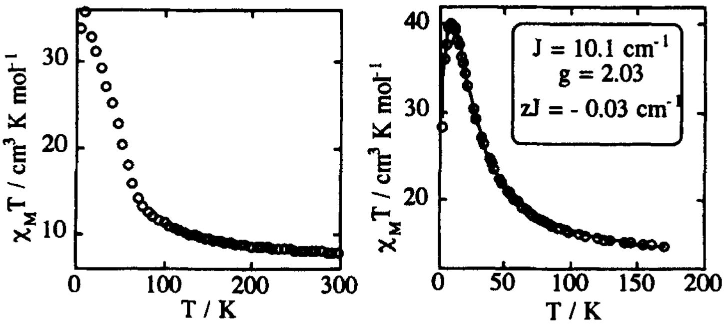


FIGURE 8 Temperature dependence of $\chi_M T$ for the pentanuclear complexes : left ligand = L_2 and right ligand = R_2.

Fitting the magnetic data leads to J_{eff} = + 5.05 cm^{-1} ; J_{CrNi} is then equal to 10.1 cm^{-1} (Fig. 8 right). This is a reasonable value for the exchange parameter between Cr^{III} and Ni^{II} through the cyanide bridge. The spin ground state of this pentanuclear compound is then S = 9 due to a ferromagnetic interaction between eleven paramagnetic centres (2 Cr^{III}, 3 Ni^{II} and six organic radicals).

CONCLUSION

A judicious choice of the nature of the ligands that chelate the peripheral metal ions led to the synthesis of two series of polynuclear complexes with spin ground states up to S = 9. The use of organic radicals as chelating ligands led to a molecule with two shells of paramagnetic centres. This rationale approach may be further extended to design squares and cubes that may contain up to 24 paramagnetic metal ions.

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