

Metal–radical approach to high spin molecules: a pentanuclear μ -cyano $\text{Cr}^{\text{III}}\text{Ni}^{\text{II}}(\text{radical})_2$ complex with a low-lying $S = 9$ ground state

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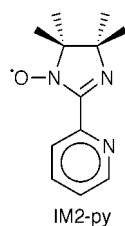
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Reacting hexacyanochromate(III) with a mononuclear Ni(II) complex chelated by two bidentate organic radicals leads to a pentanuclear complex with three different kinds of paramagnetic species interacting ferromagnetically and stabilising a high spin $S = 9$ ground state.

The metal–radical approach has been successful to design one of the first one-dimensional ferrimagnetic chains that order ferromagnetically at low temperature; nitronyl nitroxide organic radicals have been used as bis-monodentate ligands for $\text{Mn}(\text{hfac})_2$ to do so.¹ Using the same approach, it was possible to stabilise a hexanuclear ring containing six *cis*- $\text{Mn}(\text{hfac})_2$ entities connected by the phenyl nitronyl nitroxide radical and leading to a ground state $S = 12$.² Recently, Rey and coworkers reported the preparation of a bidimensionnal honeycomb like network that orders ferromagnetically at $T_C = 1.4$ K by using the bis-bidentate imidazolato nitronyl nitroxide radical as a bridging ligand for $\text{Mn}(\text{II})$ metal ions.³ Inoue and Iwamura prepared another honeycomb network using a triradical molecule to connect $\text{Mn}(\text{hfac})_2$ complexes.⁴ The first extended system containing three different paramagnetic species was reported by Kahn and coworkers.⁵

On the other hand, one of us has developed a step-by-step approach using $[\text{Cr}(\text{CN})_6]^{3-}$ as a template to assemble mononuclear Ni(II) and Mn(II) complexes bearing pentadentate ligands as blocking chelates. Two high spin molecules, $\text{Cr}^{\text{III}}\text{Ni}^{\text{II}}_6$ and $\text{Cr}^{\text{III}}\text{Mn}^{\text{II}}_6$, possessing spin ground states $S = 15/2$ and $27/2$, respectively, were thus designed.^{6,7}



By combining these two approaches, we have designed a polynuclear molecule using a new mononuclear Ni(II) complex bearing two pyridine imino nitroxide bidentate ligands IM2-py [IM2-py = 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy]⁸ acting simultaneously (i) as bulky chelates to preclude the formation of an extended network and (ii) as an extra shell of paramagnetic species to enhance the value of the spin ground state. The nature of the different components $[\text{Cr}(\text{CN})_6]$, Ni(II), IM2-py has been chosen to realise ferromagnetic interaction between the paramagnetic species in order to stabilise the highest spin state as the ground state.

A solution of the free radical IM2-Py (2×10^{-3} mol) in 30 ml of acetonitrile was added dropwise to 20 ml of acetonitrile containing $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ (1×10^{-3} mol). A precipitate appeared immediately which was filtered off, washed with acetonitrile and dried under vacuum.[†] Elemental analysis

indicated the formula $[\text{Ni}(\text{IM2-py})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \dagger$. The second step consisted in reacting $[\text{NBu}_4]_3[\text{Cr}(\text{CN})_6]$ with the Ni(II) complex in water to give a bright red precipitate immediately. The best yield was obtained for a Ni:Cr stoichiometric ratio of 3:2. Elemental analysis[‡] and thermogravimetric analysis fit well with the presence of two $\text{Cr}(\text{CN})_6$ for three $\text{Ni}(\text{IM2-py})_2$ and seven water molecules which corresponds to the formula $[\text{Cr}(\text{CN})_6]_2[\text{Ni}(\text{IM2-py})_2]_3 \cdot 7\text{H}_2\text{O}$. The IR spectrum of the new species presents all the features expected for the organic radical as well as two bands at 2160 and 2128 cm^{-1} corresponding to the elongation asymmetric vibrations of bridged⁶ and non-bridged cyanides, respectively. The new compound is soluble in most common solvents but is insoluble in water as expected for a neutral species. Unfortunately, crystals suitable for X-rays analysis were not obtained. However, the UV–VIS spectrum (MeOH, $c = 3 \times 10^{-2}$ mol l^{-1}) presents a band assigned to the ${}^3\text{T}_{2g} \leftarrow {}^3\text{A}_{2g}$ transition of the Ni(II) chromophores ($E = 11\,363$ cm^{-1} , $\epsilon = 35.9$ $\text{l mol}^{-1} \text{cm}^{-1}$) which is shifted to higher energy in comparison to that of the mononuclear $[\text{Ni}(\text{IM2-py})_2(\text{H}_2\text{O})_2]^{2+}$ complex ($E = 10\,416$ cm^{-1} , $\epsilon = 45$ $\text{l mol}^{-1} \text{cm}^{-1}$). Since the nitrogen end of the cyanide induces a stronger crystal field than water,¹² we deduce that the observed solubility is not due to some decomposition of an extended network in solution but to the fact that the compound is composed of soluble discrete polynuclear species retaining the same structure (presence of bridging cyanides) in solution as found in the solid state. The structure proposed is that of a pentanuclear complex where three *cis*- $\text{Ni}(\text{IM2-py})_2$ molecules act as bridges for two $\text{Cr}(\text{CN})_6^{3-}$ entities as depicted in Fig. 1. This structure[¶] is actually based on that of the pentanuclear complex $[\text{Fe}(\text{CN})_6]_2[\text{Ni}(\text{bpm})_2]_3 \cdot 7\text{H}_2\text{O}$ [bpm = bis(1-pyridyl)methane] described recently by Murray and coworkers.¹³

In order to check our assumption on the structure and to investigate the nature of the ground state, we carried out

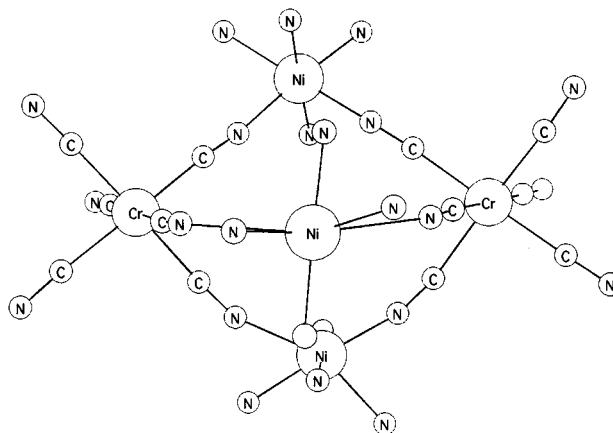


Fig. 1 Proposed model for the structure of the pentanuclear complex. Only the first coordination sphere of the nickel atoms is represented.

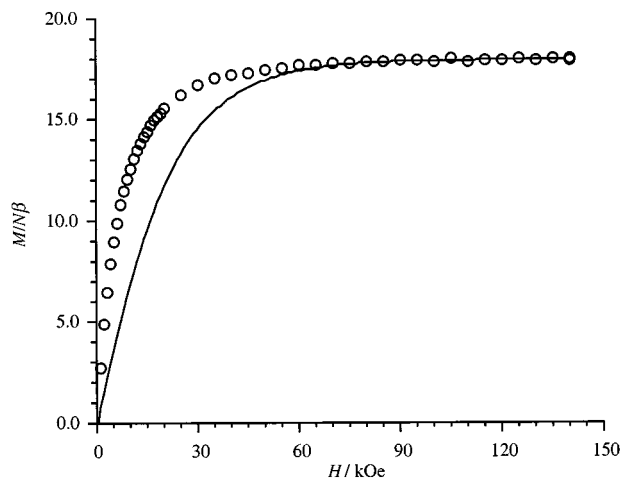


Fig. 2 M vs. H plot at $T = 2.2$ K (○) experimental, (—) sum of the calculated Brillouin functions for two $S = 3/2$ (Cr^{III} , $g_{\text{Cr}} = 1.98$), three $S = 1$ (Ni^{II} , $g_{\text{Ni}} = 2.07$) and six $S = 1/2$ (radical, $g_{\text{Rad}} = 2.00$).

magnetisation measurements on a powdered sample. The magnetisation vs. field plot (Fig. 2) ($T = 2.2$ K, $H = 0$ –140 kOe) shows that the value at saturation ($18.1 \mu_{\text{B}}$) corresponds to the expected value for ferromagnetic interaction between Cr(III) and Ni(II) on the one hand and between Ni(II) and the organic radicals on the other. Susceptibility vs. temperature measurements were carried with an applied field $H = 2$ kOe in the temperature range 300–30 K and at $H = 30$ Oe below 30 K to avoid saturation. On cooling, $\chi_{\text{M}}T$ increases and reaches a maximum at $T = 6.5$ K, then decreases (Fig. 3). The $\chi_{\text{M}}T$ value at the maximum ($42 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) is very close to that expected for an $S = 9$ ground state ($45 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for an average g value of 2) which corresponds to the parallel alignment of the local spins of the eleven paramagnetic species. In order to extract the exchange coupling parameters from the experimental data, a home-made routine was used to perform a calculation^{||} of $\chi_{\text{M}}T$ as a function of temperature for different values of J_{CrNi} and J_{NiRad} by setting the local g values to $g_{\text{Cr}} = 1.98$, $g_{\text{Ni}} = 2.07$ and $g_{\text{Rad}} = 2.00$. The calculated curves for $J_{\text{NiRad}} = 150$ K (105 cm^{-1}) and $J_{\text{CrNi}} = 9, 11, 13, 15$ and 17 K are shown in the inset of Fig. 3. The best agreement between the experimental and the calculated data is obtained, in the temperature range 300–8 K, for $J_{\text{CrNi}} = 13$ K (9 cm^{-1}) and $J_{\text{NiRad}} = 150$ K (105 cm^{-1}). It is possible at this level to introduce a parameter θ that takes into account the decrease of $\chi_{\text{M}}T$ at low temperature as due to antiferromagnetic intermolecular interactions.** a very good agreement is obtained with $\theta = -0.45$ K (Fig. 3). The sign and the values of the

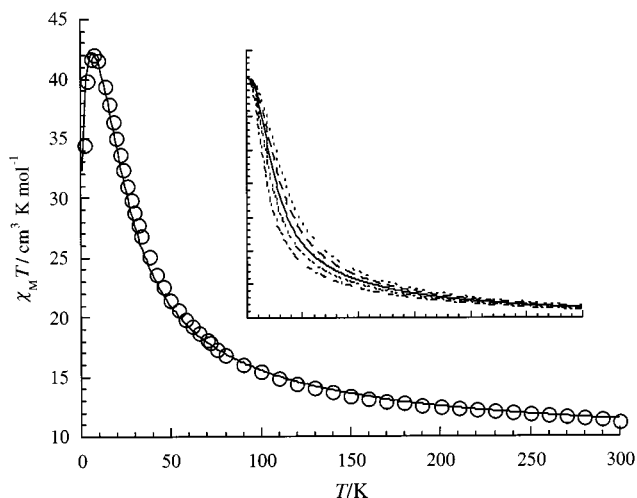


Fig. 3 $\chi_{\text{M}}T$ vs. T plot (○) experimental, (—) calculated for $J_{\text{CrNi}} = 150$ K and $J_{\text{NiRad}} = 13$ K. Inset: calculated $\chi_{\text{M}}T$ vs. T curves.

exchange coupling parameters are in the same range as have already been found for CrNi_6 ($J_{\text{CrNi}} = 15 \text{ cm}^{-1}$)⁶ and $\text{Ni}(\text{hfac})_2(\text{IM2-py})$ ($J_{\text{NiRad}} = 128 \text{ cm}^{-1}$)⁹

We are currently working on this combined strategy to design new high-spin molecules using bidentate organic radicals not only as a peripheral paramagnetic shell but also as bridging ligands.

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Notes and references

† **CAUTION:** perchlorate salts should be used in small quantities and handled with care; explosion may occur.

‡ Anal. Found (calc.) for $\text{C}_{24}\text{H}_{36}\text{N}_6\text{Cl}_2\text{O}_{12}\text{Ni}$: C, 39.80(39.48); H, 5.02(4.97); N, 11.62(11.51); Cl, 9.85(9.71); Ni, 7.80(8.03)%. The IM2-py radical is assumed to act as a bidentate ligand via its two nitrogen atoms as has already been observed for $\text{Ni}(\text{hfac})_2(\text{IM2-py})$ ⁹ and $\text{Cu}(\text{hfac})_2(\text{IM2-py})$.¹⁰ This is reasonable since the imino nitrogen atom is a much better Lewis base than the oxygen atom of the nitroxide group. The preferred isomer of this complex is *cis* because steric hindrance between the bulky ligands preclude their presence in the same plane as is the case for $\text{Ni}(\text{bipy})_2\text{Cl}_2$.¹¹

§ Anal. Found (calc.) for $\text{C}_{84}\text{H}_{110}\text{N}_{30}\text{O}_{13}\text{Ni}_3\text{Cr}_2$: C, 49.85(49.74); H, 5.32(5.46); N, 20.86(20.71); Ni, 8.57(8.68); Cr, 4.97(5.12)%.

¶ Corey–Pauling–Koltun (CPK) molecular models were used to demonstrate the absence of any steric hindrance between the ligands' methyl groups in the proposed structure.

|| The quantity $\chi_{\text{M}}T$ is related to the fluctuation of the magnetisation M , which is calculated from the energy eigenvalues and spin eigenfunctions. The eigensystem solution has been achieved by diagonalising the energy matrix. For our compound the number of microstates is given by $(2S_{\text{Cr}} + 1)^2 \times (2S_{\text{Ni}} + 1)^3 \times (2S_{\text{Rad}} + 1)^6 = 27\,648$. However, the matrices are built from the spin function basis in the M_S sub-spaces, where M_S is the z -component of the spin quantum number S . In this case, the size of the largest matrix that must be diagonalised which corresponds to the $M_S = 0$ subspace is 4390×4390 .

** ac Susceptibility measurements which were performed down to 100 mK show the absence of long-range magnetic order, a behaviour different from the ferromagnetic order found for Murray's pentanuclear complex $[\text{Fe}(\text{CN})_6]_2[\text{Ni}(\text{bpm})_2]_3 \cdot 7\text{H}_2\text{O}$. The decrease of $\chi_{\text{M}}T$ may be due to a zero-field splitting effect and not to intermolecular antiferromagnetic interaction. Unfortunately, zero-field splitting could not be included owing to prohibitive calculation times.

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