# A Heptanuclear $Cr^{III}Ni^{II}_6$ Complex with a Low-lying $S = 15/2$ Ground State

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A low-lying $S = 15/2$ ground state in a heptanuclear $Cr^{III}Ni^{II}_6$ species arises from the ferromagnetic interaction ($J = 16.8$ cm$^{-1}$) between one central $Cr^{III}$ ($S = 3/2$) and six peripheral $Ni^{II}$ ($S = 1$) ions through the cyanide bridge.

One of the synthetic challenges in the field of molecular magnetism is the design of polynuclear discrete entities with high-spin ground states.[1–3] These systems belong to a new class of materials exhibiting original magnetic properties. A $Mn_{12}$ cluster[4] with an $S = 10$ ground state was shown recently to present striking magnetic properties at very low temperatures which deserve to be studied further in other systems. High-spin ($S = 9/2$) molecules[5,6] and two molecular-based magnets[7,8] containing the $Cr^{III}$–L–$Ni^{II}$ sequence† were obtained owing to the ferromagnetic interaction between the spin carriers. We report here on a $Cr^{III}Ni^{II}_6$ heptanuclear bimetallic cyanide bridged system $[Cr\{(CN)Ni(tetren)\}_6](ClO_4)_9$ **1** (tetren = tetraethylenepentamine) which exhibits an $S = 15/2$ ground state arising from the ferromagnetic interaction between a central $Cr^{III}$ ($S = 3/2$) and six peripheral $Ni^{II}$ ($S = 1$) ions through the cyanide bridge.

Tetren is a pentadentate ligand able to block five coordination sites around the potentially octahedral $Ni^{II}$ ion, leaving one coordination site occupied by a water molecule. Compound **1** was obtained by dropwise addition of an aqueous solution of freshly prepared $K_3[Cr(CN)_6]\cdot 2H_2O$ ($5 \times 10^{-4}$ mol in 20 ml) to an aqueous solution of $[Ni(tetren)(H_2O)](ClO_4)_2$ ($6 \times 10^{-3}$ mol in 50 ml).‡ Prismatic pink–yellowish crystals appeared within two weeks when the solution was left to evaporate. Satisfactory elemental analysis (Cr, Ni, C, H, N, Cl) for $C_{54}H_{138}Cl_9CrN_{36}Ni_6O_{36}$ **1** was obtained. The IR spectrum in the 2000–2200 cm$^{-1}$ region shows a single band at 2150 cm$^{-1}$ resulting from the high frequency shift of the chromicyanide $\nu_{as}$ $CN^-$ stretching band. This is indicative of the occurence of the $Cr^{III}$–CN–$Ni^{II}$ sequence[7] in **1**. Up to now, no single crystals suitable for complete refining of the crystallographic structure are available. The skeleton of **1** is depicted in Fig. 1.

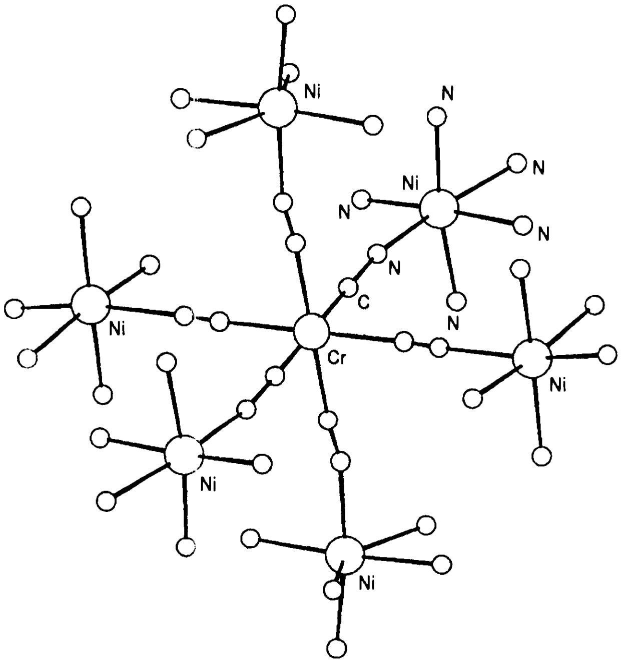

**Fig. 1** Schematic view of **1**, tetren is represented by its five nitrogen atoms

The magnetic measurements were performed using a SQUID susceptometer. The $\chi_MT$ thermal dependence for **1** is shown in Fig. 2, $\chi_M$ being the magnetic molar susceptibility. The high temperature value of $\chi_MT$ (9.74 cm$^3$ mol$^{-1}$ K at $T = 246$ K) is higher than expected for noninteracting $Cr^{III}$ and $Ni^{II}$ metal ions (7.87 cm$^3$ mol$^{-1}$ K, calculated with a mean $g = 2$). Upon cooling, $\chi_MT$ increases sharply below $T = 50$ K and reaches a maximum (32 cm$^3$ mol$^{-1}$ K) at $T = 6$ K. $\chi_MT_{max}$ corresponds to what is expected for a low-lying $S = 15/2$ spin state with $g = 2$. The slight decrease of $\chi_MT$ below 6 K can be due either to zero-field splitting of $Ni^{II}$ or to intermolecular interactions. The $\chi_MT$ value at $T = 6$ K and the absence of minima in the $\chi_MT = f(T)$ curve are in agreement with a ferromagnetic interaction between the $Cr^{III}$ and the $Ni^{II}$ ions. The $\chi_MT$ experimental data were fitted to the analytical expression obtained by using the spin hamiltonian:

$$\mathcal{H} = -J_{NiCr}[\hat{S}_{Ni(1)} + \hat{S}_{Ni(2)} + \hat{S}_{Ni(3)} + \hat{S}_{Ni(4)} + \hat{S}_{Ni(5)} + \hat{S}_{Ni(6)}]\cdot\hat{S}_{Cr} + \beta g\{[\hat{S}_{Ni(1)} + \hat{S}_{Ni(2)} + \hat{S}_{Ni(3)} + \hat{S}_{Ni(4)} + \hat{S}_{Ni(5)} + \hat{S}_{Ni(6)}] + \hat{S}_{Cr}\}\cdot H$$

where the interaction between the $Ni^{II}$ ions and the zero-field splitting associated with $Ni^{II}$ are assumed to be negligible in comparison to the $Cr^{III}$–$Ni^{II}$ intramolecular exchange parameter $J_{NiCr}$. The best fit parameters are: $J_{NiCr} = +16.8$ cm$^{-1}$ and $g_{Ni} = g_{Cr} = 2.00$ ($R = 6.9 \times 10^{-4}$). {$R$ is defined as $\Sigma[(\chi_MT)_{calc} - (\chi_MT)_{obs}]^2/\Sigma[(\chi_MT)_{obs}]^2$}.

Since at $T = 6$ K, the first excited state is well separated from the ground state,§ magnetization measurements as a function of the magnetic field can be used in order to confirm the $S = 15/2$ value of the low-lying ground state. A saturation value of 14.42 $\mu_B$ ($T = 6$ K) is observed in the plot of $M/N\beta$ *vs.* $H$ presented in Fig. 3. The fit of the experimental data to the Brillouin function[9] for an $S = 15/2$ spin state gives a $g_{15/2}$ value of 1.97 ($R = 6.8 \times 10^{-5}$). The magnetization *vs.* field theoretical curve corresponding to one $Cr^{III}$ and six $Ni^{II}$ magnetically isolated ions lies well below that due to **1**. All these data confirm the occurrence of a low-lying $S = 15/2$ spin ground state due to the $Cr^{III}$–$Ni^{II}$ ferromagnetic interaction through the cyanide bridges in **1**.

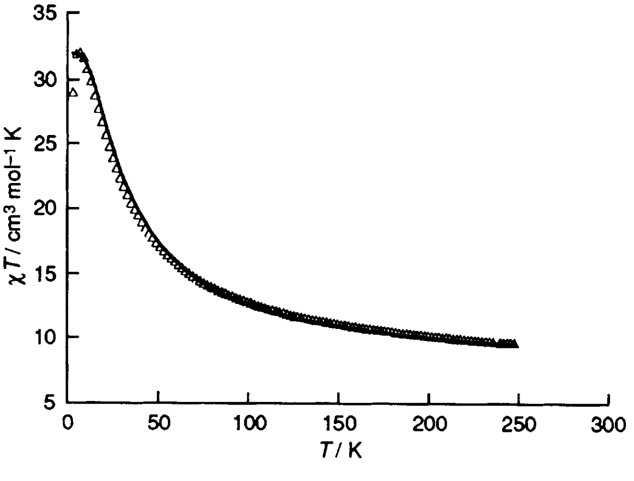

**Fig. 2** Plot of $\chi_MT = f(T)$; (△) experimental data, (—) best fit, $J = 16.8$ cm$^{-1}$, $g = 2.00$, $R = 6.9 \times 10^{-4}$

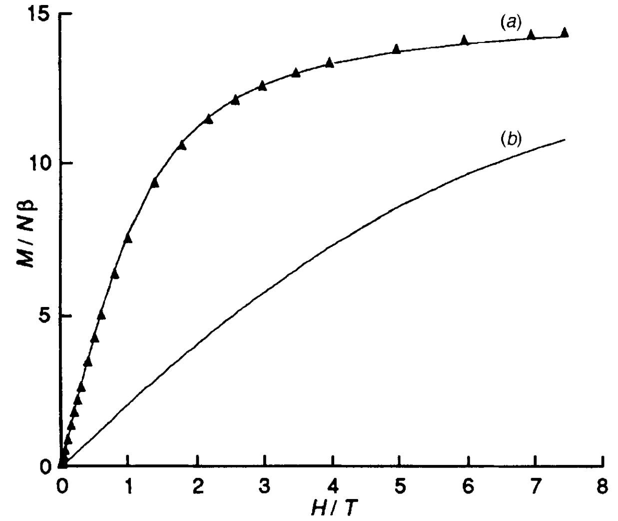

**Fig. 3** Plot of $M = f(H)$ at $T = 6$ K; (▲) experimental data, (*a*) best fit, (*b*) Brillouin function corresponding to one Cr$^{III}$ ($S = 3/2$) and six Ni$^{II}$ ($S = 1$) magnetically isolated ions. $g_{15/2} = 1.97$, $S = 15/2$

Hexacyanochromate(III) has shown to be a versatile building-block for the design of tridimensional (3D) extended networks.[7,10–12] We have showed here that it can be used to design an heptanuclear system which is a valuable model for 3D materials. The magnitude of the ferromagnetic interaction through the cyanide bridge has been determined and found to be quite important for two metal ions more than 5 Å apart. Up to now few high-spin molecules exist; using the same synthetic strategy it will be possible to design similar heptanuclear complexes with higher spin ground states¶ that may play an important role in the development of the emerging area of mesoscopic compounds.

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## Footnotes

† L can be a bisbidentate ($C_2O_4^{2-}$ or $C_2O_2S_2^{2-}$) or a bismonodentate ($CN^-$) ligand.

‡ An aqueous solution of $[Ni(tetren)H_2O](ClO_4)_2$ was prepared by adding 6.2 × $10^{-3}$ mol of tetren to 6 × $10^{-3}$ mol of $Ni(ClO_4)_2 \cdot 6H_2O$.

§ The energy gap between the ground and the first excited low-lying states is $3J/2$ (22.5 cm$^{-1}$), and at $T = 6$ K the thermal energy $kT$ is about 4.2 cm$^{-1}$.

¶ Using Fe$^{II}$ or Mn$^{II}$ instead of Ni$^{II}$, it is possible to obtain systems with low-lying ground states $S = 21/2$ and 27/2, respectively.

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