One step assembly of a nonanuclear $Cr^{III}_2Ni^{II}_7$ bimetallic cyanide bridged complex†

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The reaction of hexacyanochromate with connectivity 6 and a mononuclear Ni complex bearing a bulky tridentate macrocycle leads in one step to the formation of a nonanuclear Cr_2Ni_7 complex with central low spin and peripheral high spin Ni ions; fast tunnelling of the magnetization is observed at low temperature by micro-SQUID studies on a single crystal.

During the last 10 years, much effort has been devoted to the preparation of polynuclear complexes using hexacyanometallates as building blocks. One of the objectives is to provide molecules that possess a high spin ground state and may behave as Single Molecule Magnets (SMM) with tunnelling of the magnetization at low temperature.[1–3]

High nuclearity (larger then seven) complexes are difficult to obtain with hexacyanometallates as building blocks. Heptanuclear complexes can be stabilized when the "complex as metal" that reacts with the hexacyanometallate has only one available site.[2] In most cases, extended networks are favored for kinetic reasons. Cyanide bridged molecules with higher nuclearities were recently reported with *fac*-$LM(CN)_3$ type complexes as building blocks.[4] The only example of a hexacyanometallate based complex with nuclearity higher than seven was recently reported by Dunbar and coworkers.[5]

In this communication, we report on the preparation and the magnetic behavior of a nonanuclear cyanide bridged Cr_2Ni_7 complex with hexacyanochromate as building block. A judicious choice of the "complex as metal" and the nature of the solvent is required in order to keep the species soluble until the thermodynamic conditions are achieved.[6] The complex $(iPrtacn)NiCl_2$ (iPrtacn stands for 1,4,7-tris-isopropyl-1,4,7-triazacyclononane) was selected to be the "complex as metal" because (i) it has three potentially available sites to coordinate the cyanide's nitrogen atoms and (ii) the ligand has bulky groups that favor the solubility of molecular species in organic solvents.‡ The reaction was carried out in methanol and the insoluble $K_3Cr(CN)_6$ compound was used as the source of hexacyanometallate. Within a few hours at ambient conditions, the dissolution of $K_3Cr(CN)_6$ was complete and upon the addition of sodium tetraphenylborate to the mother solution, a green precipitate was isolated.§ Single crystals suitable for X-ray analysis were obtained by recrystallizing the powder from acetone/THF with a yield of over 70%. The complex crystallizes in the monoclinic $P2_1/n$ space group.¶ The crystal structure analysis shows that the compound consists of a nonanuclear complex cation, four tetraphenyl borate counter-anions and solvent molecules with the formula $[(Cr(CN)_6)_2(Ni(iPrtacn))_3(Ni(iPrtacn)Cl)_4](BPh_4)_4{\cdot}H_2O,CH_3OH,C_4H_8O,4C_3H_6O$. The core of the complex has a trigonal bipyramid shape (Fig. 1 and Fig. S1). The base of the bipyramid is occupied by three Ni atoms and the two apical positions by two chromium. The metal centers are bridged by the cyanide ligands. Each chromium is linked to two other Ni atoms by two bridging cyanides.

The geometry around the Cr atoms is almost isotropic; the C–N distances for the cyanide ligands are almost identical and range from 1.14 to 1.16 Å. The NiNC angles (NC stands for the cyanide bridge) are all larger than 169° apart from the Ni6–N810–C810

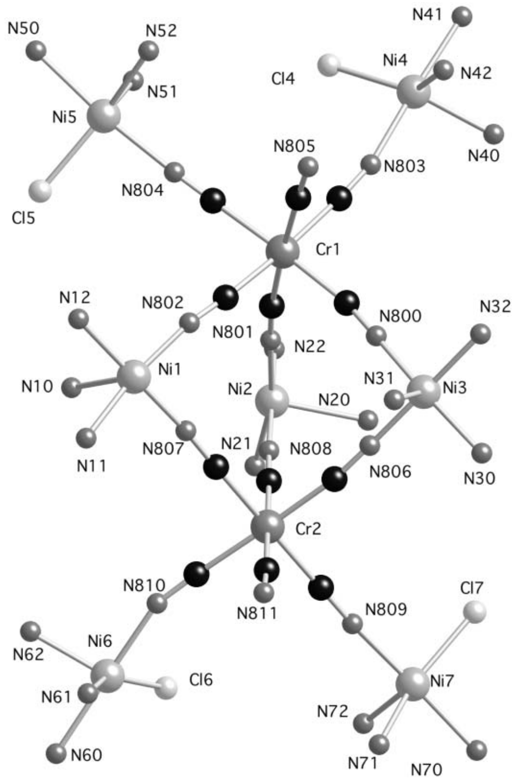

Fig. 1 View of the molecular structure of the nonanuclear complex, only the first coordination sphere of the metal ions is depicted for clarity (see ESI).

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† Electronic supplementary information (ESI) available: drawing of the structure of the complex and that of the mononuclear Ni units, $1/\chi_M = f(T)$, $M = f(H)$ and $\chi_M T$ expression. See DOI: 10.1039/b514053f

angle which is equal to 161.86°. The 7 Ni atoms are crystallographically independent. They are pentacoordinated, however the geometry around the peripheral Ni atoms is close to a trigonal bipyramid while the central Ni atoms have a geometry much closer to a square pyramid (sp) (Fig. S2).

For the peripheral Ni atoms, the base of the tbp is occupied by a chloride atom and by two nitrogen atoms from the iPrtacn ligand, the apical positions are occupied one by the third nitrogen atom of the organic ligand and the other by the bridging nitrogen of the cyanide. The geometries around the four peripheral Ni atoms are almost the same (we describe here that of Ni7). The N809–Ni7–N70 angle is almost linear (176.31°). The main distortion from the tbp geometry is due to the angles within the base of the tbp. The N71–Ni7–N72 bite angle of the iPrtacn ligand is equal to 87.35°. The N72–Ni7–Cl17 and the N71–Ni7–Cl17 angles are equal to 118.24° and 153.37° respectively. The Ni–N distances correspond to what is expected, they range from 2.03 to 2.18 Å. The Ni7–Cl7 distance is equal to 2.28 Å. The central Ni atoms have a geometry much closer to a square pyramid. The base of the pyramid is occupied by two cyanides' nitrogen atoms (N801 and N808) and two amines' nitrogen (N22 and N21); the apical position is occupied by the remaining nitrogen atom of the organic ligand (N20). The shortest Ni–N bond lengths are those with the nitrogen atoms of the cyanide bridges (1.88–1.90 Å). The other two Ni–N distances in the base of the sp are slightly longer (2.00–2.02 Å) while the bond length between Ni and the nitrogen atom occupying the apical position is much longer (2.30 Å).

The magnetic studies show that upon cooling from room temperature, $\chi_M T$ increases from a value of 9.35 cm^3 mol^{-1} K, reaches a maximum (16.35 cm^3 mol^{-1} K) at T = 12 K and then decreases (Fig. 2). The overall behavior of $\chi_M T$ with temperature is consistent with the presence of intramolecular ferromagnetic exchange coupling interactions as expected for quasi-linear Cr^{III}–CN–Ni^{II} linkages.[2a,8] The decrease below 13 K is due, as we will see below, to zero field splitting (ZFS) within the ground state and weak intermolecular antiferromagnetic interactions. The value at room temperature (9.35 cm^3 mol^{-1} K) is lower than expected for 7 Ni^{II} (S = 1) and 2 Cr^{III} (S = 3/2) uncoupled ions (13.22 cm^3 mol^{-1} K assuming g_{Ni} = 2.2 and g_{Cr} = 2.00). Furthermore, the maximum value is well below the 55 cm^3 mol^{-1} K expected for an S = 10 ground state resulting from the ferromagnetic interaction between the 2 Cr^{III} and 7 Ni^{II} paramagnetic ions.

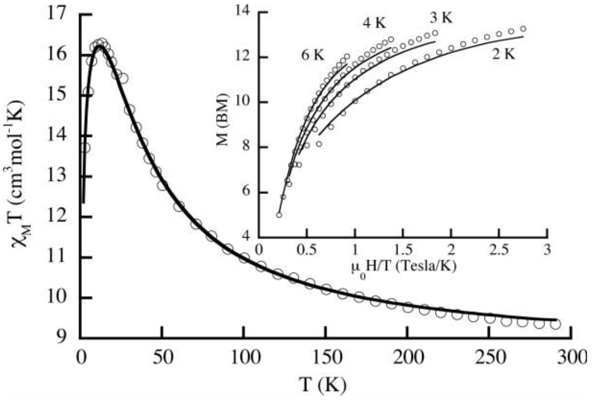

Fig. 2 $\chi_M T$ = f(T) and M = f(H/T) (inset) for **1**·H$_2$O, (○) experimental data and (—) best fit.

The magnetization *vs.* field studies at T = 2 K lead at H = 5.5 Tesla to a maximum value of 13.26 Bohr Magnetons (BM), well below the 20 BM expected for an S = 10 ground state (Fig. 2, inset). These data show clearly that some electronic spins are missing. The analysis of the $1/\chi_M$ = f(T) curve above T = 200 K shows that the nonanuclear complex contains only four paramagnetic Ni^{II} centers, the other three seem to be diamagnetic (see Fig. S3).[9] A close look at the structure of the nonanuclear complex shows that the central Ni atoms have rather short Ni–N bond lengths within the plane of the pyramid (as low as 1.86 Å with the cyanide nitrogen atoms) and a relatively long distance with the apical atoms (2.28 Å). A reasonable assumption at this level is that the three central Ni^{II} ions are diamagnetic. Thus the nonanuclear complex must be considered as formed by two peripheral CrNi$_2$ units with S = 7/2 separated by three diamagnetic Ni^{II} ions. The $\chi_M T$ = f(T) data were then fitted considering CrNi$_2$ units and in order to reproduce the decrease of $\chi_M T$ at low temperature, intermolecular interactions between the paramagnetic CrNi$_2$ expressed by the parameter zJ were considered within the framework of the mean field approximation (see SI).[10] The best fit gives the following results ($H = -J_{CrNi} S_{Cr}\cdot(S_{Ni1} + S_{Ni2})$): J_{CrNi} = +15.6 cm^{-1}, g = 2.11, zJ = −0.05 cm^{-1} with an agreement factor $R = 9 \times 10^{-5}$.

Magnetization *vs.* field data at T = 2, 3, 4 and 6 K for fields above 0.5 Tesla (in order to overcome the antiferromagnetic intermolecular interactions) can be fitted with the same model *i.e.* isolated CrNi$_2$ units with S = 7/2 state.[11] The fit leads to $D_{7/2}$ = −0.67 cm^{-1}, E/D = 0.15 and g = 1.97 ($R = 9 \times 10^{-4}$) (Fig. 2, inset). Having a good idea of the magnitude of the ZFS parameter, it is possible now to fit the $\chi_M T$ = f(T) data by imposing the value of the ZFS parameter found from the M = f($\mu_0 H/T$) data. The best fit leads to the following parameters (only one J parameter turned out to be sufficient): J_{CrNi} = +15.3 cm^{-1}, g = 2.11, zJ = −0.04 cm^{-1} and $D_{7/2}$ (fixed) = −0.67 cm^{-1} ($R = 2 \times 10^{-4}$) (Fig. 2). Thus, weak antiferromagnetic interactions between the CrNi$_2$ entities (within and between the nonanuclear complexes) responsible for the S = 7/2 ground state, do operate at low temperature since one cannot reproduce the $\chi_M T$ behavior below 12 K only with the ZFS parameter obtained from the magnetization data or by considering only an antiferromagnetic interaction between the CrNi$_2$ units within the Cr$_2$Ni$_7$ complexes.

Since one of the requirements to observe the blocking of the magnetization (negative D value for the S = 7/2 ground state) is achieved,[1] the magnetic properties at low temperature were investigated. Magnetization studies on one single crystal using an array of micro-SQUIDs (the field is parallel to the easy magnetic axis of the crystal) were carried out at temperatures below 1 K. Firstly, the sample was cooled in the presence of a magnetic field and the field cycled between −1.4 and 1.4 Tesla at a sweep rate of 0.017 Tesla/s at different temperatures (Fig. S4). Below T = 0.2 K, a strong transition is observed at zero field which may be due to the tunnelling of the magnetization. In order to confirm this hypothesis, the sample was cooled in zero field and then the field was cycled between 0 and 1.4 Tesla at different sweep rates (Fig. 3). In such an experiment and in the case of a fast tunnelling regime, one may expect the following behavior. At zero field, half of the molecules are in the M_S = S state (the other half in the M_S = −S

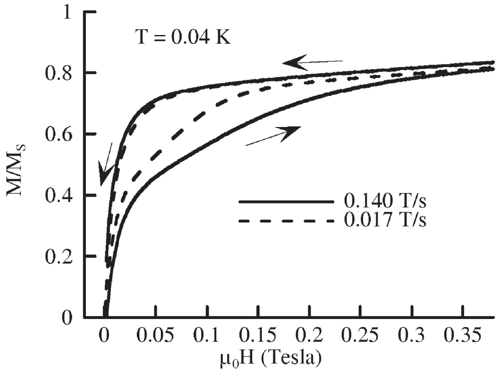

Fig. 3 Magnetization *vs.* field at $T = 0.04$ K with two different sweep rates. The sample was cooled in zero field.

state). On increasing the field with a high sweep rate (0.14 Tesla/s), half of the molecules are blocked in the up state and are not able to tunnel which leads to the hysteresis loop. When the field is increased more slowly (0.017 Tesla/s), part of the molecules in the up state are able to tunnel, the transition at zero field is stronger and the hysteresis loop is narrower (Fig. 3). This is what we observe for the present complex. Since SMMs are defined as complexes that present a blocking of the magnetization at zero applied field (slow relaxation), the present complex is not (strictly) a SMM.

In this communication, we have shown that using hexacyanometallates may lead to high nuclearity complexes providing a judicious choice of the "complex as metal" molecules. The behavior at very low temperature is intriguing since half integer spin systems (Kramer doublets) are supposed not to show tunnelling at zero field. However, the presence of intermolecular interactions (dipolar, exchange, ...) may lead to such behavior. A detailed study of the intermolecular interactions (with pressure for instance) may cast light on the origin of the zero field tunnelling at low temperature.

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Notes and references

‡ Synthesis of Ni(iPrtacn)Cl_2: iPrtacn was synthesised according to published procedures.[7] The iPrtacnNiCl_2 complex was prepared as follows: 0.46 g (2×10^{-3} M) of $NiCl_2 \cdot 6H_2O$ were dissolved in 10 ml of methanol, 2 ml of trimethyl orthoformate were added and the solution mixed with 30 ml of DME and 100 ml of THF. It was then heated under reflux for 10 minutes. Then 0.5 g (2×10^{-3} M) of iPrtacn were dissolved in 20 ml of THF and added dropwise to the first solution. A green-yellowish precipitate appeared upon cooling the solution. The precipitate was filtered and then dissolved in a minimum amount of chloroform and precipitated by adding an excess of THF. The solid was filtered, thoroughly washed with THF and dried under vacuum. Elemental analysis: % exp: C 46.45, H 8.77, N 10.99, Cl 18.39, Ni 14.96; calc. for $C_{15}H_{33}Cl_2Ni$ C 46.79, H 8.64, N 10.91, Cl 18.42, Ni 15.24. Yield, 90%.

§ Synthesis of $[(Cr(CN)_6)_2(Ni(iPrtacn))_3(Ni(iPrtacn)Cl)_4](BPh_4)_4 \cdot H_2O$ (**1**·$(BPh_4)_4 \cdot H_2O$): 100 mg (0.26×10^{-3} mol) of Ni(iPrtacn)Cl_2 were dissolved in 20 ml of methanol, then 24 mg (0.075×10^{-3} mol) of $K_3[Cr(CN)_6]$ were added as solid to the nickel solution. The color of the solution quickly started to change from yellow to green and after a few hours all the solid was dissolved. 177 mg (0.52×10^{-3} mol) of $NaBPh_4$ dissolved in 20 ml of methanol were added dropwise. A green precipitate appeared, which was filtered, washed with methanol and dried under vacuum. Single crystals were obtained by slow evaporation of an acetone solution of the powder containing a very small amount of THF. Yield on crystals 70%. IR: ν(CN) = 2159 cm^{-1}. Elemental analysis was performed on dried ground single crystals. Anal. % exp C 62.68, H 7.85, N 11.31, Cr 2.55, Ni 9.87, Cl 3.08; calc. for **1**·$(BPh_4)_4 \cdot H_2O$ C 63.14, H 7.79, N 11.41, Cr 2.57, Ni 10.14, Cl 3.5.

¶ X-Ray data collection for $[(Cr(CN)_6)_2(Ni(iPrtacn))_3(Ni(iPrtacn)Cl)_4]$-$(BPh_4)_4 \cdot H_2O,CH_3OH,C_4H_8O,4C_3H_6O$ ($C_{230}H_{349}B_4Cl_4Cr_2N_{33}Ni_7O_7$) (38 H atoms belonging to the solvent molecules were not refined), crystal dimensions $0.10 \times 0.08 \times 0.05$ mm, monoclinic, $P2_1/n$, $a = 26.3093(14)$, $b = 26.2548(13)$, $c = 36.3513(18)$ Å, $\beta = 108.828(2)°$, $V = 23766(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.215$ g cm^{-3}, $\mu = 0.734$ mm^{-1}, $F(000) = 9177$, $\theta_{max} = 24.83°$, $T = 100$ K, structure solution with SIR97,[12] refinement against $F2$ (SHELXL97[13]) with anisotropic thermal parameters for all non-hydrogen atoms except solvent molecules, calculated hydrogen positions with riding isotropic thermal parameters. 181309 data collected, 37510 unique data, 24476 data with $I > 2\sigma(I)$, 2514 parameters refined and 24 restraints for one $(BPh_4)_4$, GOF(F^2) = 1.067, final R indices $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$, $R1 = 0.0990$, $wR2 = 0.2372$, max./min. residual electron density 0.861/−0.528 e$^-$Å^{-3}. At the end of the refinement, seven solvent molecules are placed. But five peaks of residual electronic density suggest that there are still disordered solvent molecules not refined. CCDC 282789. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514053f

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