# Superparamagnetic bimetallic cyanide-bridged coordination nanoparticles with $T_B$ = 9 K†

Laure Catala,*[a] Alexandre Gloter,[b] Odile Stephan,[b] Guillaume Rogez[c] and Talal Mallah*[a]

**Dispersible, nearly isolated 6 nm nanoparticles of the $CsNiCr(CN)_6$ Prussian blue analogue coated with polyvinyl-pyrrolidone (PVP) show superparamagnetic behaviour with a relatively high blocking temperature $T_B$ = 9 K.**

Cyanide-bridged coordination networks have been widely investigated because of the large diversity of magnetic properties they present which can be tuned either by a magnetic field, light, temperature or pressure.[1] On the other hand, switchable cyanide-bridged clusters have been reported (single molecule magnets SMMs,[2a] spin crossover[2b] and photomagnetic molecules[2c]) that may be potential candidates for single molecule information storage devices. Another possible approach to magnetic objects that may lead to new bistable nanosized objects is to stabilize isolated nanoparticles of coordination networks that are easy to process and may be integrated into devices. Furthermore, an important issue is to study the relation between the size of these nanoparticles and their properties. Since Prussian blue analogue magnets have a wide range of Curie temperatures, from 9 K up to room temperature, it is of interest to achieve single domain nanoparticles of such coordination networks as rather high blocking temperatures are expected.

The first method to prepare such objects has been to restrict their growth using microemulsion applied to Prussian blue and some of its analogues.[3] Nanocubes with a size ranging from 12 to 30 nm stabilized within the inverse micelles, and organized in 2D arrays were obtained.[3b] Subsequently, using the same method, we were able to prepare 3 nm nanoparticles of $Ni[Cr(CN)_6]_{2/3}$ and isolate them as a redispersible solid by the coordination of a pyridine derivative which brings the desired solubility.[4] These particles exhibit superparamagnetic behaviour with a blocking temperature of 5.5 K for the powder and below 2 K when dispersed in PVP (2.5% in weight). Other methods using PVP, sol–gel, mesostructured silica or apoferritin have been used to stabilize nanoparticles of the Prussian blue analogues.[5–10] However, the magnetic properties have not been investigated much for most of these samples and only two compounds were clearly reported to

exhibit superparamagnetism, discarding any spin glass behaviour.[4,8]‡ In order to observe superparamagnetism with a rather high blocking temperature, one has to prepare nanoparticles of a coordination network that behaves as a magnet with a high Curie temperature. To do so, we have chosen the Prussian blue analogue ferromagnet $CsNi[Cr(CN)_6]$ that has a Curie temperature $T_C$ equal to 90 K.[11]

In this communication, we report on the preparation of 6 nm bimetallic superparamagnetic nanoparticles with a blocking temperature $T_B$ = 9 K. The nanoparticles were stabilised by PVP and found to be perfectly dispersible in various solvents.

An aqueous solution containing $NiCl_2 \cdot 6H_2O$ ([$Ni^{2+}$] = 2 mM), CsCl ([$Cs^+$] = 4 mM) and PVP K30 was first prepared in a ratio of [pyr]/[$Ni^{2+}$] = 100 (where pyr stands for the pyrrolidone monomer). A Dynamic Light Scattering (DLS) measurement on this solution revealed the presence of objects with a mean size of 8 nm which corresponds to the gyration radius of the PVP that may coordinate weakly to the divalent nickel cations.§ An equivalent volume of a 2 mM aqueous solution of $K_3Cr(CN)_6 \cdot 2H_2O$ was then added leading to a stable light green solution. Stirring the solution for one hour does not show any noticeable evolution. A DLS measurement, at this stage, shows the same size as for the first solution before adding the hexacyanochromate(III) salt. If particles have formed, their size is clearly not larger than the size of PVP in solution; the PVP envelope still determines the overall size seen by DLS. The addition of 3 volumes of acetone leads to a light green solid that was centrifuged, and dried under vacuum. The X-ray powder diffraction (XRPD) diagram confirms the fcc structure expected with a cell parameter $a$ = 10.54 Å which corresponds to the value reported for the bulk compound (Fig. S1, ESI†).[11] Furthermore, an estimated size of 6.6 ± 0.5 nm could be extracted using Scherrer's law from the XRPD diagram. The IR spectrum shows the asymmetric vibration of bridging cyanides at 2171 $cm^{-1}$ with a small peak at 2130 $cm^{-1}$ that can be assigned to free cyanides present at the surface of the particles. The presence of the polymeric chains was evidenced by the C=O broad peak at 1654 $cm^{-1}$ and C–H vibrations between 2890 and 2960 $cm^{-1}$. Elemental analysis performed on the sample gives the composition $Cs_{0.7}Ni[Cr(CN)_6]_{0.9}(pyr)_{26} \cdot 38H_2O$ **1**, which corresponds to 9% in weight of $Cs_{0.7}Ni[Cr(CN)_6]_{0.9}$ in PVP.¶ Even when completely dry, the light green solid could be perfectly dispersed in water, ethanol, methanol and chloroform. The DLS measurement obtained on a dispersion of **1** in water gave a mean size of 13 nm, showing nearly no aggregation even after the precipitation–dispersion process.‖ These data suggest that bimetallic cyanide-bridged nanoparticles embedded by PVP were indeed formed. The incomplete insertion of the $Cs^+$ cations that leads to 10% vacancies in

*[a] Laboratoire de Chimie Inorganique, UMR CNRS 8613, Université Paris-Sud, 91405 Orsay, France. E-mail: laurecatala@icmo.u-psud.fr; mallah@icmo.u-psud.fr; Fax: +33 (0)1 69 15 47 54; Tel: +33 (0)1 69 15 47 49*
*[b] Laboratoire de Physique des Solides, UMR CNRS 8502, Université de Paris-Sud, F-91405 Orsay Cedex, France*
*[c] Institut de Physique et Chimie des Matériaux de Strasbourg, UMR ULP-CNRS 7504, BP 43, 23 rue du Loess, 67034 Strasbourg cedex 2, France*
† Electronic supplementary information (ESI) available: XRPD diagram, plots of $\chi_M T = f(T)$, $1/\chi_M = \phi(T)$, $\chi_M' = f(T)$, $M = f(T)$, $\ln(\tau) = f(1/T_{max})$. See DOI: 10.1039/b516425g
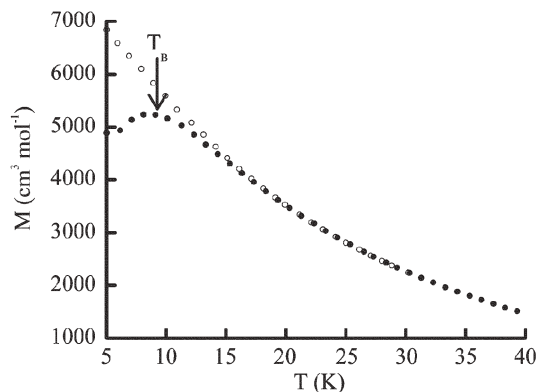
hexacyanochromate(III) may be due to the low concentration of metal ions in the solutions used to prepare the particles. The original 1 : 1 : 1 Cs : Ni : Cr compound was prepared using a different procedure where an aqueous 1 mM Ni(II) solution was added to a 10 mM solution of $KCs_2[Cr(CN)_6]$ in water.

Scanning Transmission Electron Microscopy (STEM) using dark field (Fig. 1) confirms the presence of nearly isolated nanoparticles.** A mean size of 6.4 nm was estimated on 250 particles with a standard deviation of 3.0 nm. Some of the particles have facets and can even form perfect cubes (Fig. 1, see inset). Nevertheless, statistical analysis demonstrated a slightly elongated projected shape ratio of $L/l = 1.6$ ($L = 7.0$ nm $\pm$ 3.4 nm, $l = 4.3$ nm $\pm$ 2.3 nm). Most of the particles remain isolated on the grid, with some small aggregates of two or three particles (Fig. 1, inset). This is consistent with the result observed by DLS after dispersion that gave a mean size of 13 nm in solution. Since the STEM images are indicative of the state of the compound after the solvent evaporation process, one can reasonably assume that the PVP matrix contains rather well isolated particles, with locally some weak aggregation.

Magnetic studies were performed on a solid sample of **1** using a SQUID magnetometer operating in the 2–300 K temperature range between 0 and 5.5 T. The $\chi_M T$ vs. temperature plot at an applied field of 5000 Oe (Fig. S2, ESI†) shows that, upon cooling, $\chi_M T$ increases slowly from room temperature to 100 K and then abruptly to reach a maximum value of 180 cm$^3$ K mol$^{-1}$ at $T = 56$ K before decreasing. The high temperature behaviour indicates the presence of a ferromagnetic exchange coupling interaction between Cr(III) and Ni(II) as expected.[11] The fit of the $1/\chi_M = f(T)$ curve (Fig. S3, ESI†) in the 200–300 K temperature range leads to a positive $\theta$ value (105 K) and to a Curie constant $C = 2.87$ cm$^3$ K mol$^{-1}$, consistent with the expected value for isolated metal ions considering $g_{Cr} = 2.0$ and $g_{Ni} = 2.1$. The value of 4.8 $\mu_B$ found for the magnetic moment at saturation measured at $T = 2$ K (Fig. S4, ESI†) is in good agreement with the expected value for a ferromagnetic interaction between the metal ions. In order to check the behaviour of the nanoparticles below $T = 100$ K that corresponds to the abrupt increase of $\chi_M T$, field cooled (FCM) and zero-field cooled (ZFCM) magnetization measurements were carried out in the 100–2 K temperature range. The two curves diverge below $T = 14$ K and a maximum of the ZFCM curve is observed at 9 K (Fig. 2). This behaviour may be due to a ferromagnetic order or to a blocking of the magnetization. The
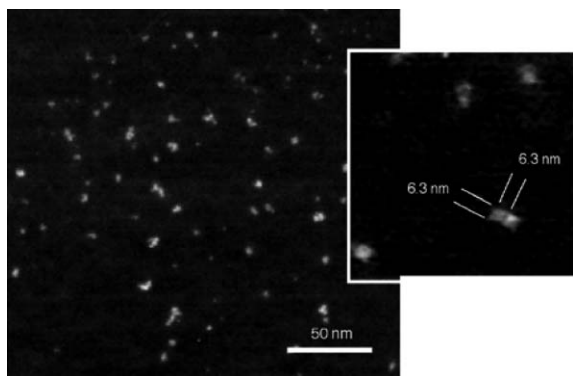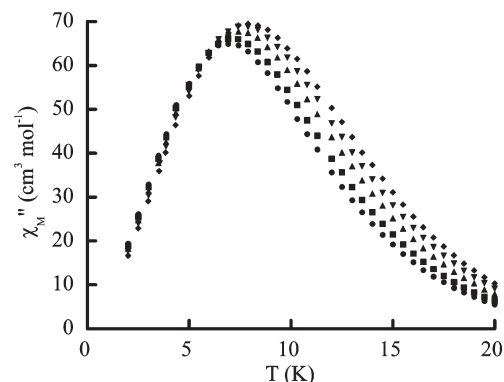


**Fig. 2** Field cooled (O) and zero-field cooled (●) magnetizations for **1**.

latter assumption is reasonable since the CsNi[Cr(CN)$_6$] bulk compound orders at $T_C = 90$ K and the Ni$_3$[Cr(CN)$_6$]$_2$ one at 40 K.

In order to confirm the blocking of the magnetization and the magnetic single-domain nature of the particles, ac susceptibility measurements were performed in zero applied dc field and a 3 Oe oscillating field at five different frequencies ($v$) between 50 and 1000 Hz. A frequency dependent behaviour of the in-phase susceptibility $\chi'$ (Fig. S5, ESI†) and the out-of-phase susceptibility $\chi''$ is observed (Fig. 3). The anisotropy energy barrier $\Delta = 166$ K and the preexponential factor $\tau_0 = 1.1 \times 10^{-13}$ s could be extracted from the $\ln(\tau) = f(1/T_{max})$ (where $\tau = 1/2\pi v = \tau_0\exp(\Delta/kT_{max})$, $\tau_0$ is the relaxation time at infinite temperature and $T_{max}$ is the temperature of the maximum of the $\chi'' = f(T)$ curves) (Fig. S6, ESI†). The parameter $\Phi = 0.11$ is characteristic of superparamagnetic nanoparticles and discards any spin glass-like behaviour for which $\Phi < 0.1$.††[12] The magnetization recorded at $T = 2$ K reveals a hysteretic behaviour with a coercive field of 80 Oe (Fig. 4). The remnant magnetization at $T = 2$ K is about 25% of the value at saturation.

In this communication, we have shown that 6 nm nearly isolated nanoparticles of Cs$_{0.7}$Ni[Cr(CN)$_6$]$_{0.9}$ can be produced coated with PVP and dispersed in various solvents. Moreover, we have shown that they behave as single domain magnetic objects with the highest blocking temperature (9 K) reported for fully characterized coordination nanoparticles. It has to be pointed out that this blocking temperature corresponds to nearly isolated particles, and that higher temperatures can be expected for less diluted



**Fig. 1** Dark field STEM images of the Cs$_{0.7}$Ni[Cr(CN)$_6$]$_{0.9}$ nanoparticles coated by PVP and zoom on an aggregate of two nanoparticles.



**Fig. 3** Thermal variation of the out-of-phase ($\chi_M''$) component of the ac susceptibility at 50 (●), 100 (■), 250 (▲), 500 (▼) and 1000 (=) Hz for **1**.
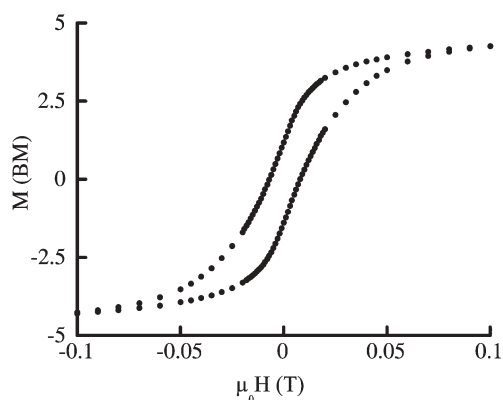
**Fig. 4** Magnetization *vs.* field at *T* = 2 K for **1**.

composites or if the particles are organized in two dimensions. Raising the blocking temperature of such coordination nanoparticles while keeping a similar size can be achieved by using other Prussian blue analogues that possess higher Curie temperatures. This work is underway in our group.

## Notes and references

‡ Compounds in ref. 5 were reported to have frequency dependence of the out-of-phase component of the susceptibility, yet the characteristic parameters $\Phi$ and $\tau_0$ used to discriminate superparamagnetic behaviour from spin glass were not reported.

§ Dynamic Light Scattering measurements were performed on a Malvern Nanosizer Apparatus (equipped with a backscattering mode) on 1.5 mL of an aqueous solution. The volume profile was used to estimate the size corresponding to the main peaks bearing in mind it underestimates the proportion of smaller particles. It is used in our work as a qualitative measurement of the size of particles or aggregates in solution, which includes systematically a solvation shell and the organic shell in the case of the protected particles. It provides a comparative measurement between particles before precipitation and after dispersion to know the amount of aggregation.

¶ Elemental analysis: exp Cs 2.31, Ni 1.52, Cr 1.25, C 49.34, H 47.72, N 11.25. Calc. for $Cs_{0.7}Ni[Cr(CN)_6]_{0.9}\{C_6H_9N\}_{26}\{H_2O\}_{38}$ Cs 2.38, Ni 1.50, Cr 1.19, C 49.56, H 7.92, N 11.24.

‖ The mean size of 13 nm may be the result of one to two particles embedded in PVP compared to 8 nm seen before precipitation

** STEM experiments have been done using a dedicated cold FEG STEM VG HB05. High angle annular dark field images have been recorded using a collection angle above 60 mrad and an acquisition time of around 15 s per image. The obtained contrast was sufficient to determine the particle contours. Geometrical parameters for each isolated particle have then been obtained using DM 3.4 Gatan software. EELS (Electron Energy Loss Spectroscopy) experiments (not shown) have also confirmed the presence of C, N, Cr, Cs and Ni in the nanoparticles.

†† $\Phi = (T_{max} - T_{min})/(T_{max}(v_{max} - v_{min}))$ where $T_{max}$ and $T_{min}$ are the maxima of the $\chi''$ curves obtained at $v_{max}$ and $v_{min}$ which are the extreme values of the frequencies applied during the experiment.[12]

1 See for example: E. Coronado, M. C. Gimenez-Lopez, G. Levchenko, F. M. Romero, V. Garcia-Baonza, A. Milner and M. Paz-Pasternak, *J. Am. Chem. Soc.*, 2005, **127**, 4580; O. Sato, T. Iyoda, A. Fujishima and K. Hashimoto, *Science*, 1996, **272**, 704; M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier and F. Villain, *Coord. Chem. Rev.*, 1999, **192**, 1023; H. Tokoro, S. Ohkoshi, T. Matsuda and K. Hashimoto, *Inorg. Chem.*, 2004, **43**, 5231; Y. Arimoto, S. Ohkoshi, Z. J. Zhong, H. Seino, Y. Mizobe and K. Hashimoto, *J. Am. Chem. Soc.*, 2003, **125**, 9240; S. Ohkoshi, H. Tokoro and K. Hashimoto, *Coord. Chem. Rev.*, 2005, **249**, 1830; W. Kosaka, K. Nomura, K. Hashimoto and S. I. Ohkoshi, *J. Am. Chem. Soc.*, 2005, **127**, 8590; A. Dei, *Angew. Chem., Int. Ed.*, 2005, **44**, 1160; V. Niel, M. C. Munoz, A. B. Gaspar, A. Galet, G. Levchenko and J. A. Real, *Chem.–Eur. J.*, 2002, **8**, 2446; V. Niel, J. M. Martinez-Agudo, M. C. Munoz, A. B. Gaspar and J. A. Real, *Inorg. Chem.*, 2001, **40**, 3838; S. Bonhommeau, G. Molnar, A. Galet, A. Zwick, J.-A. Real, J. J. McGarvey and A. Bousseksou, *Angew. Chem., Int. Ed.*, 2005, **44**, 4069.
2 (*a*) See for example: L. M. C. Beltran and J. R. Long, *Acc. Chem. Res.*, 2005, **38**, 325; C. P. Berlinguette, D. Vaughan, C. Canada-Vilalta, J. R. Galan-Mascaros and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 2003, **42**, 1523; H. Miyasaka, H. Takahashi, T. Madanbashi, K.-I. Suguira, R. Clérac and H. Nojiri, *Inorg. Chem.*, 2005, **44**, 5969; D. F. Li, S. Parkin, G. B. Wang, G. T. Yee, A. V. Prosvirin and S. M. Holmes, *Inorg. Chem.*, 2005, **44**, 4903; (*b*) M. Nihei, M. Ui, M. Yokota, L. Q. Han, A. Maeda, H. Kishida, H. Okamoto and H. Oshio, *Angew. Chem., Int. Ed.*, 2005, **44**, 6484; (*c*) J. M. Herrera, V. Marvaud, M. Verdaguer, J. Marrot, M. Kalisz and C. Mathonière, *Angew. Chem., Int. Ed.*, 2003, **43**, 5468; . Mathonière, R. Podgajny, P. Guionneau, C. Labrugère and B. Sieklucka, *Chem. Mater.*, 2005, **17**, 442.
3 (*a*) S. P. Moulik, G. C. De, A. K. Panda, B. B. Bhowmik and A. R. Das, *Langmuir*, 1999, **15**, 8361; (*b*) S. Vaucher, M. Li and S. Mann, *Angew. Chem.*, 2000, **39**, 1793; (*c*) S. Vaucher, J. Fielden, M. Li, E. Dujardin and S. Mann, *Nano Lett.*, 2002, **2**, 225; (*d*) E. Dujardin and S. Mann, *Adv. Mater.*, 2004, **16**, 1125.
4 L. Catala, T. Gacoin, J.-P. Boilot, É. Rivière, C. Paulsen, E. Lhotel and T. Mallah, *Adv. Mater.*, 2003, **15**, 826.
5 T. Uemura and S. Kitawaga, *J. Am. Chem. Soc.*, 2003, **125**, 7814; T. Uemura, M. Ohba and S. Kitagawa, *Inorg. Chem.*, 2004, **43**, 7339; T. Uemura and S. Kitawaga, *Chem. Lett.*, 2005, **34**, 132.
6 L. Catala, C. Mathonière, A. Gloter, O. Stephan, T. Gacoin, J.-P. Boilot and T. Mallah, *Chem. Commun.*, 2005, **6**, 746.
7 N. Bagkar, R. Ganguly, S. Choudhury, P. A. Hassan, S. Sawant and J. V. Yakhmi, *J. Mater. Chem.*, 2004, **14**, 1430; M. H. Cao, X. L. Wu, X. Y. He and C.W. Hu, *Chem. Commun.*, 2005, **17**, 2241; H. L. Sun, H. T. Shi, F. Zhao, L. M. Qi and S. Gao, *Chem. Commun.*, 2005, **34**, 4339; Q. Kong, X. G. Chen and J. L. Yao, *Nanotechnology*, 2005, **16**, 164.
8 J. G. Moore, E. J. Lochner, C. Ramsey, N. S. Dalal and A. E. Stiegman, *Angew. Chem., Int. Ed.*, 2003, **42**, 2741.
9 G. Clavel, Y. Guari, J. Larionova and C. Guerin, *New J. Chem.*, 2005, **29**, 275.
10 J. M. Dominguez-Vera and E. Colacio, *Inorg. Chem.*, 2003, **42**, 6983; N. Gálvez, P. Sánchez and J. M. Domínguez-Vera, *Dalton Trans.*, 2005, **15**, 2492.
11 V. Gadet, T. Mallah, I. Castro, M. Verdaguer and P. Veillet, *J. Am. Chem. Soc.*, 1992, **114**, 9213.
12 See for example on spin-glass-like Prussian blue analogues: W. E. Buschmann, J. Ensling, P. Gutlich and J. S. Miller, *Chem.–Eur. J.*, 1999, **5**, 3019 and references therein.