A Prussian Blue Nanomolecule: Crystal Structure and Low-Temperature Magnetism

G. Rogez,[†] S. Parsons,[‡] C. Paulsen,[§] V. Villar,[§] and T. Mallah*,[†]

Laboratoire de Chimie Inorganique, UMR CNRS 8613, Université Paris-Sud, 91405 Orsay, France, Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, U.K. EH9 3JJ, and Centre de Recherche sur les Très Basses Températures, CNRS, F-38054 Grenoble, France

Received March 27, 2001

Since the beginning of the 1990s, the elaboration of discrete species containing a large number of interacting magnetic centers has been boosted by the discovery of single-molecule magnets.[1] A rational approach to the preparation of such discrete species that possess a large-spin ground state consists of organizing around a central complex (complex-ligand) a first shell of paramagnetic centers. If the peripheral paramagnetic centers are metallic ions that play the role of Lewis acids toward the central unit, they must be capped by an organic ligand in order to prevent polymerization. The number of metallic centers in the first shell is determined by the "connectivity" of the complex-ligand. Kahn and Gatteschi were the first to prepare high-spin molecules ($S = {}^{9}/_{2}$) using oxalate- and oxamidate-based complex-ligands of connectivity 2 and 3.[2] We have extended this approach using hexacyanochromate(III) as a complex-ligand (connectivity 6) and prepared the two heptanuclear complexes $[Cr(CNNi(tetren))_6]^{9+}$ and $[Cr(CNMn(trispeecmen))_6]^{9+}$ that possess larger spin ground states $S = {}^{15}/_{2}$ and ${}^{27}/_{2}$, respectively.[3] Using the same approach, Spiccia et al. reported very recently the structure of a compound containing the heptanuclear cationic $[Cr(CNMn(dmptacn))_6]^{9+}$ species and the mononuclear $Cr(CN)_6^{3-}$ as a countercation.[4] In a different project, a one-pot approach allowed the preparation of octacyanometalate-based high-spin molecules $(M^{V}(CN)_8)_9$-$(Mn^{II}(ROH)_3)_6$ ($M = W$, $R = CH_3$,[5] and $M = Mo$, $R = C_2H_5$[6]) that possess fully capped cubane structures and the highest spin states reported to date, $S = {}^{39}/_{2}$ and ${}^{51}/_{2}$, for tungsten and molybdenum, respectively.

The oldest and one of the most fascinating coordination compounds is Prussian blue. Prussian blue is a mixed-valence cyanide-bridged cubic network containing low-spin Fe^{II} ($S = 0$) surrounded by carbon and high-spin Fe^{III} ($S = {}^{5}/_{2}$) linked to the nitrogen atoms of the cyanide bridge.[7] It orders ferromagnetically below $T_C = 5.6$ K.[8] We have used our rational approach to prepare a discrete species that has the same local structure and electronic properties as Prussian blue. In a first report we have shown that the reaction of Fe^{III}(salmeten)Cl with $K_4[Fe(CN)_6]$ leads to the formation of the heptanuclear compound $[Fe^{II}(CNFe^{III}(salmeten))_6]Cl_2{\cdot}6H_2O$. The complex possesses an intervalence band, and the magnetic properties revealed a ferromagnetic interaction between the high-spin Fe^{III} as in the parent Prussian blue.[9]

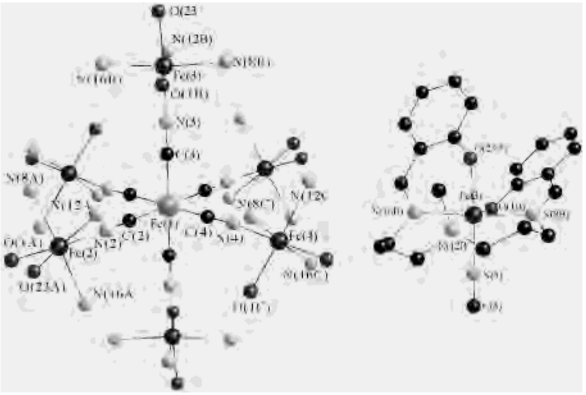

Figure 1. Left: View of the heptanuclear complex $FeFe_6^{2+}$; only the nearest neighbors of the metal ions are shown for clarity. Right: View of the mononuclear unit Fe(salmeten)NC showing the conformation of the ligand.

We report here the crystal structure and the very low magnetic behavior of a similar compound containing the same heptanuclear complex, i.e., $[Fe^{II}(CNFe^{III}(salmeten))_6]Cl_2{\cdot}17.25CH_3OH$ (for Fe(salmeten) see Figure 1, right).

Blue plates are obtained within 2 months when an aerobic solution of $K_4[Fe(CN)_6]$ in a 1/10 H_2O/CH_3OH mixture is left to diffuse in an H-tube into a methanolic solution of Fe(salmeten)-Cl. X-ray diffraction studies[10] reveal the presence of a heptanuclear dication complex $FeFe_6^{2+}$ and the Cl^- anion. The heptanuclear species has an inversion center (Figure 1). The Fe(1)−C distances are in the range 1.881(4)−1.892(4) Å, the Fe(1)−C−N angles found to be in the range 178.4(3)−179.3(3)° deviate only slightly from linearity, and the C(cyanide)−N(cyanide) bond distances range between 1.154(4) and 1.147(4) Å. These are the structural characteristics one may expect for a ferrocyanide unit.[11,12] The geometry around the peripheral Fe^{III} ions is distorted due the nature of the salmeten pentadentate ligand.

[†] Université Paris-Sud.

[‡] University of Edinburgh.

[§] CRTBT.

(1) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A.-L.; Brunel, L. C.; Guillot, M. *J. Am. Chem. Soc.* **1991**, *113*, 5873. Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. *J. Am. Chem. Soc.* **1993**, *115*, 1804. Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. Gatteschi, D.; Caneschi, A.; Pardi, L.; Sessoli, R. *Science* **1994**, *265*, 1054. Eppley, H. J.; Tsai, H.-L.; de Vries, N.; Folting, K.; Christou, G.; Hendrickson, D. *J. Am. Chem. Soc.* **1995**, *117*, 301. Aubin, S. M. J.; Wemple, M. W.; Adams, D. M.; Tsai, H.-L.; Christou, G.; Hendrickson, D. **1996**, *118*, 7746.

(2) Pei, Y.; Journaux, Y.; Kahn, O.; Dei, A.; Gatteschi, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1300. Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1988**, *27*, 399. Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1989**, *28*, 100.

(3) Mallah, T.; Auberger, C.; Verdaguer, M.; Veillet, P. *J. Chem. Soc., Chem. Commun.* **1995**, 61. Scuiller, A.; Mallah, T.; Nivorozkhin, A.; Tholence, J.-L.; Verdaguer, M.; Veillet, P. *New J. Chem.* **1996**, *20*, 1.

(4) Parker, R. J.; Spiccia, L.; Berry, K. J.; Fallon, G. D.; Moubaraki, B.; Murray, K. S. *Chem. Commun.* **2001**, 333.

(5) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoshi, S.-I.; Hashimoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 2952.

(6) Larionova, J.; Gross, M.; Pilkington, M.; Audres, H.; Stoeckli-Evans, H.; Güdel, H. U.; Descurtins, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1605.

(7) Buser, H. J.; Schwarzenbach, D.; Petter, W.; Ludi, A. *Inorg. Chem.* **1977**, *16*, 2704.

(8) Buser, H. J.; Ludi, A.; Fisher, P.; Studach, T.; Dale, B. W. *Z. Phys. Chem.* **1974**, *92*, 354. Ito, A.; Suenaga, M.; Ono, K. *J. Chem. Phys.* **1968**, *48*, 3597.

(9) Rogez, G.; Marvilliers, A.; Rivière, E.; Audière, J.-P.; Lloret, F.; Varret, F.; Goujon, A.; Mendenez, N.; Girerd, J.-J.; Mallah, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 1605.

(10) Crystal data for $[Fe(CNFe(salmeten))_6]Cl_2{\cdot}17.25MeOH$: $M = 3279.33$, monoclinic, $P2_1/n$, $a = 21.40(2)$ Å, $b = 17.761(18)$ Å, $c = 22.05(2)$ Å, $V = 8164(14)$ Å^3, $\beta = 103.06(2)°$, $T = 220(2)$ K, $Z = 2$, 46590 reflections measured, of which 16826 were unique ($R_{int} = 0.0739$). The structure was solved by direct methods (SIR92) and refined with Shelxl-97. The final conventional *R*-factor [based on *F* and 8620 data with $F > 4\sigma(F)$] was 0.0552.

10.1021/ic015528z CCC: $20.00

The distances between the six Fe^{III} atoms and their surrounding atoms are almost the same within the heptanuclear complex. The $Fe^{III}-O$(phenolate) distances range from 1.919(3) to 1.959(3) Å. The distances between Fe^{III} and the imine nitrogen atoms are in the range 2.092(4)−2.112(4) Å. They are shorter than those with the tertiary amine of salmeten which range from 2.279(4) to 2.308(4) Å. The shortest bond distances around Fe^{III} are those corresponding to the cyanide nitrogen atoms (2.027(4)−2.049(4) Å). They are in the same range as the $Fe^{III}-N$ distances found in Prussian blue (2.01−2.04 Å).[7] It is worth noting that the conformation adopted by salmeten around Fe^{III} leads to chiral Fe(salmeten)NC moieties (Figure 1, right). But because of the presence of an inversion center on the central Fe^{II}, the two enantiomers coexist in the coordination sphere of the heptanuclear complex. The distance between two Fe^{III} ions in trans of the central Fe^{II} is around 10.2 Å. The largest distance between two atoms within the complex is more than 2 nm.

The heptanuclear species may be considered from the structural point of view as a model for the oldest coordination compound Prussian blue. We have already shown that from the electronic point of view it is also the case because of the presence of an intervalence band and especially because the interaction between the six high-spin $S = {}^5/_2$ Fe^{III} is ferromagnetic.[9] The expected spin ground state for the isolated cluster should then be equal to 15. However, at $T = 2$ K, the $\chi_M T$ curve has a maximum with a value equal to 35 $cm^3\ mol^{-1}$ K, which means that either many low-lying spin states are still populated at this temperature (due to an extremely weak $Fe^{III}-Fe^{III}$ ferromagnetic interaction for instance) or an intermolecular antiferromagnetic interaction is operative within the compound. Magnetization versus field and ac susceptibility measurements were thus carried out below 2 K.

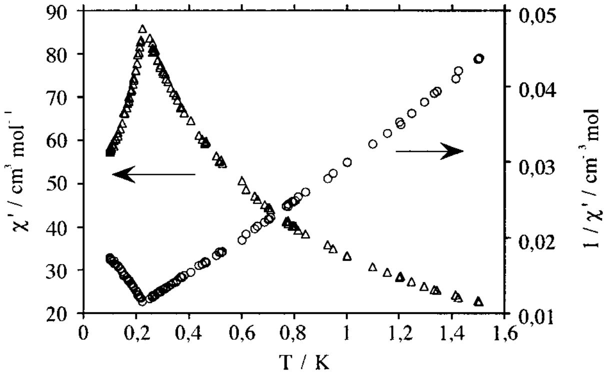

Figure 2. Thermal dependence of the real susceptibility (△) and its inverse (○) at $f = 12.34$ Hz in zero applied dc field.

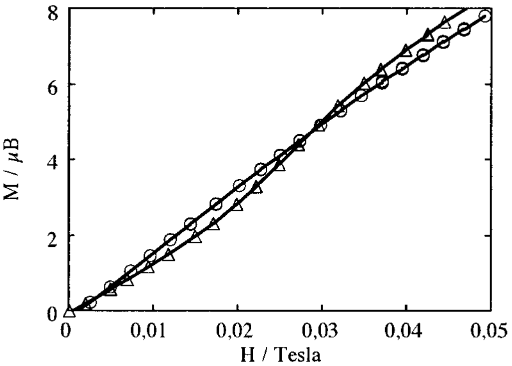

Figure 3. Magnetization vs field plot at $T = 90$ (Δ) and 230 mK (O).

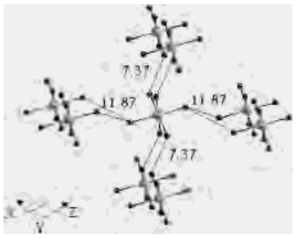

Figure 4. Shortest $Fe^{III}-Fe^{III}$ distances belonging to different complexes; the large gray dots are Fe^{II} ions, and the small black ones are Fe^{III}. Only the metal ions are depicted for clarity.

Ac susceptibility measurements were performed in the 1.5−0.1 K temperature range at different frequencies (0.12, 1.24, and 12.37 Hz) of the oscillating field in zero dc magnetic field. The absence of out of phase susceptibility (χ'') response and the fact that the real susceptibilities (χ') have no frequency dependence together with the shape of the $\chi' = f(T)$ and $1/\chi' = f(T)$[13] curves are in line with the occurrence of an antiferromagnetic order at $T_N = 220$ mK (Figure 2). This is confirmed when examining the $M = f(H)$ curve in the low-field region performed at $T = 90$ mK (below the ordering temperature) which presents a sigmoidal shape (Figure 3) characteristic of a metamagnetic behavior.[14] The critical field H_C (taken at the inflection point of the $M = f(H)$ plot) corresponding to the transition from the antiferromagnetic phase to the induced ferromagnetic phase (at $T = 90$ mK) is equal to 300 Oe.[14] The sigmoidal shape of the curve vanishes at $T = 230$ mK (above the ordering temperature) as expected for a metamagnet.[14] A saturation value of 30 μB is reached at high field (not shown here), confirming the presence of six $S = {}^5/_2$ magnetic centers as expected. The magnetic energy responsible for the antiferromagnetic coupling, given by $g\beta H_C$, is equal to 0.03 cm^{-1} (assuming $g = 2$). The mean field approach allows one to estimate the extent of the antiferromagnetic interaction between the heptanuclear species by equating the magnetic energy $g\beta H_C$ with $z|J|S$ where S is the spin of the interacting entities, z the number of one entity's nearest neighbors, and J the exchange coupling interaction between the polynuclear species. z may be taken to be equal to 8 since each heptanuclear species is surrounded by eight other species with shortest intermolecular distances (taken between peripheral Fe^{III} complexes) of 7.37 and 11.87 Å (Figure 4). If we assume $S = 15$, the $|J|$ value can be estimated to be equal to 2.5×10^{-4} cm^{-1}.

We have shown here that the absence of the observation of the $S = 15$ spin ground state expected from the intramolecular ferromagnetic exchange coupling is due to the presence of intermolecular antiferromagnetic interaction between the heptanuclear species. This antiferromagnetic interaction precludes the observation of the magnetic properties inherent to one molecule like the blocking of the magnetization for instance. To wipe out the intermolecular interactions between the molecular species, solid dilution of the $FeFe_6^{2+}$ species with diamagnetic $Fe^{II}Ga^{III}{}_6{}^{2+}$ is currently in progress in our laboratory.

Acknowledgment. We thank the CNRS (Centre National de Recherche Scientifique) and the European community for financial support (Contract HPRN-CT-1999-00012/TMR Network "MolNanoMag").

Supporting Information Available: Crystallographic information for $[Fe^{II}(CNFe^{III}(salmeten)_6]Cl_2 \cdot 17.25CH_3OH$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC015528Z

---

(11) Swanson, B. I.; Hamburg, S. I.; Ryan, R. R. *Inorg. Chem.* **1974**, *13*, 1685. Pierrot, M.; Kern, R.; Weiss, R. *Acta Crystallogr.* **1966**, *20*, 425.

(12) Ohba, M.; Maruono, N.; Okawa, H.; Enoki, T.; Latour, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 11566. Miyasaka, H.; Matsumoto, N.; Okawa, H.; Re, N.; Gallo, A.; Floriani, C. *J. Am. Chem. Soc.* **1996**, *118*, 981. Re, N.; Crescenzi, R.; Floriani, C.; Miyasaka, H.; Matsumoto, N. *Inorg. Chem.* **1998**, *37*, 2717.

(13) Fitting the linear part (above $T = 220$ mK) of the $1/\chi' = f(T)$ curve to the Curie−Weiss expression $1/\chi = (T - \theta)/C$ leads to a negative θ value of −0.24 K.

(14) Marvilliers, A.; Parsons, S.; Rivière, E.; Audière, J.-P.; Kurmoo, M.; Mallah, T. *Eur. J. Inorg. Chem.* **2001**, 1287.