Hexacyanometalate Molecular Chemistry: Trinuclear CrNi$_2$ Complexes; MicroSQUID Magnetisation Studies of Intermolecular Interactions

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(Dated: March 22, 2022)

Three different CrNi$_2$ complexes were synthesized. They differ from each other by the nature of the terminal ligand and of the counter anion: [Cr(CN)$_4$(CN-Ni(tetren))]$_2$Cl, that crystallizes in two different crystallographic systems and [Cr(CN)$_4$(CN-Ni(dienpy)$_2$)]$_2$(ClO$_4$). The ground state spin value is 7/2 for the three systems (ferromagnetic interaction between chromium(III) and nickel(II) ions). The magnetisation of the three CrNi$_2$ complexes was measured using an array of micro-SQUIDs in a temperature range between 0.04 K and 7 K, under a magnetic field up to 1 T. The three samples present a three dimensional magnetic ordering. The correlation between the structure and the intermolecular coupling is analysed in terms of steric hindrances of the terminal ligand, orientation of the molecules in the unit cell (canted structure) and crystal symmetry.

PACS numbers: PACS numbers: 75.45.+j, 75.60.Ej

1. Introduction

The search for new polynuclear molecules displaying high spin ground state and anisotropy raises the interest of synthetic chemists $^{1,2,3,4,5,6}$ and physicists $^{7,8,9}$ involved in the field of molecular magnetism $^{10,11}$. These anisotropic high spin molecules exhibit original magnetic properties such as single molecule magnet behaviour $^{12,13,14,15,16,17}$ (long relaxation time for the magnetisation below a so-called blocking temperature, $T_B$) or magnetic quantum tunnelling effect $^{18,19}$. Our research approach is devoted to the synthesis of such complexes in order to get single molecule.

In order to understand the single molecule magnet (SMM) behaviour, it is important to remind that a phenomenological Hamiltonian correlated to a spin state diagram might describe all polynuclear complexes. In presence of a uniaxial anisotropy, a zero-field splitting is observed which splits the ground state in 2S + 1 levels. The activation energy of the anisotropy barrier, $E_a$, between the spin states $M_S = S$, is a direct function of D (uniaxial anisotropy) and S (ground state spin value), $E_a = -DS^2$. To obtain a single molecule magnet i.e. to avoid a rapid relaxation process, the spin as well as the absolute value of the anisotropy have to be as high as possible and D has to be negative so that the state of highest $M_S$ lies below in energy. The exchange coupling J between two spin carriers has to be important to well separate the ground state from the first excited states. The intermolecular interaction, $J_{\text{inter}}$, plays also an essential role: it has to be negligible, necessary condition to avoid a three-dimensional magnetic ordering and to observe the properties of an isolated nanoscale object. Very few examples of clusters responding to all these criteria have been described in the literature, among them Mn$_{12}$ $^{14,15,20}$, Fe$_8$ $^{21}$ and Mn$_4$ $^{22}$ are reference compounds.

To obtain anisotropic high spin molecules, we developed a step by step synthetic strategy based on the coupling reaction of polycyanometalate precursors (viewed as Lewis bases) and mononuclear complexes of transition metal ions with a polydentate ligand, leaving a unique accessible position only (as Lewis acids) $^{22,23,24}$. Starting with hexacyanometalate precursors, this strategy allows to obtain: i) isotropic high spin molecules such as CrCu$_6$ ($S = 9/2$), CrNi$_6$ ($S = 15/2$) and CrMn$_6$ ($S = 27/2$) $^{24}$; ii) complexes with various structural anisotropy but low ground state spin, for instance CoNi$_4$ ($S = 1$), CoNi$_3$ ($S = 1$) and CoNi$_5$ ($S = 1$) or even singlets CoNi$_2$ ($S = 0$) and CoNi$_6$ ($S = 0$) $^{25}$; iii) anisotropic high spin molecules like CrNi ($S$...
and orthorhombic, space group = Pbc2. In the present paper, different CrNi complexes ([Cr(CN)4](CN-Ni(L))2, L being a polydentate ligand) are investigated below 2K in order to search a potential single molecule magnet behaviour or to evaluate the intermolecular magnetic exchange interaction. After presenting briefly the structural parameters of the various complexes, we discuss the low temperature magnetic properties on oriented single crystals and evaluate the main parameters involved in the intermolecular exchange interaction which induces the three-dimensional ordering at very low temperature (See also Ref. 28, 29, 30).

2. CrNi complexes, presentation and structure
Five different [Cr(CN)4](CN-Ni(L))2+ complexes, abbreviated as CrNi in the following, have been isolated and characterised, including by single crystal X-ray diffraction. The compounds differ from each other by the nature of the polydentate ligand, L, [tetraethylendiphenyleneamine (tetren)], tris(2-aminoethyl)-N,N,N'-ethyldiamine (trenen) and bis(2-pyridylmethyl) - N, N' - diethylenetriamine (dienpy2) or by the nature of the counter anions (tetrafluoroborate, chloride or perchlorate). The magnetic studies (4-300K) indicate in all cases a ferromagnetic intramolecular interaction between the chromium and the nickel spin carriers, as predicted for orthogonal magnetic orbitals and a S = 7/2 value for the ground state. The intramolecular exchange coupling value, JCrNi, varies from + 4.5 cm^{-1} to + 10 cm^{-1} according to the distortion of the Cr-CN-Ni unit and especially to the change in the C - N - Ni angle. The uniaxial anisotropy, D, computed from fitting of the susceptibility data, is around - 0.3 cm^{-1}. High-field EPR experiments are in progress in order to determine precisely the anisotropy factor. The synthesis, the characterisation, the magnetic properties and magneto-structural correlation studies of these species are presented elsewhere 24.

Three of the five complexes are involved in the present study: i) [Cr(CN)4](CN-Ni(tetren))2Cl, noted CrNi2(tetren) that crystallizes in two different crystallographic systems: monoclinic, space group = P21/c and orthorhombic, space group = Pbc21, named 1 and 1* respectively; ii) [Cr(CN)4](CN-Ni(dienpy2))2(ClO4) that crystallizes in the monoclinic system, space group = C2/c, noted CrNi2(dienpy2) or 3. This compound is formed with a bulky ligand that influences the intermolecular distance and the intermolecular exchange coupling. The two cationic complexes are presented in figure 1. The CrNi(tetren) monoclinic system 1, forms pink distorted hexagonal crystals. The hexagonal face corresponds to the (1 0 0) crystallographic plane. The three others faces are the (1-1 1), (1-1-1) and (1 1-1) planes. In the crystal, the molecules are aligned in a two-dimensional sheet, parallel to the (1 0 0) plane. The planes are separated by the counter anions, Cl\(^{-}\) and wa-

FIG. 2: Temperature dependence of the hysteresis loops, measured for two perpendicular directions in (100) plane. The temperatures are indicated. In Figure 2a (above) the field is applied along the easy axis and the behaviour is typical of a system with ferromagnetic intermolecular coupling. In Figure 2b (below), the field is applied perpendicular to the easy axis and the hysteresis loops present an antiferromagnetic plateau.
FIG. 3: Temperature dependence of the magnetic susceptibility in the two orthogonal directions of Fig. 2. The dashed lines represent the fit with a Curie-Weiss law. Parallel to the easy axis (figure 3a, above), a positive Curie-Weiss constant is observed, (+ 0.6 K, ferromagnetic coupling). Perpendicular to the easy axis (figure 4b, below) the Curie-Weiss constant is negative (- 0.25 K, antiferromagnetic coupling).

angle of 90° between the molecular Ni-Cr-Ni axes. As in the previous case, the chloride ions and the hydrogen bond network formed by the water molecules separate the molecular layers.

Finally, the crystals obtain from the CrNi$_2$(dienpy)$_2$ system, 3, are red-pink parallelepipeds that belong to the monoclinic system. The molecules are aligned in a two dimensional arrangement and the planes are separated by the ClO$_4$-counterions. The orientations of the molecules in the crystal are very similar to the one observed in compound 1. Despite the facts that the dienpy$_2$ ligand, due to the presence of pyridine rings, is more bulky than the tetren ligand and that the perchlorate is bigger than chloride, the intermolecular distances in 3 are only slightly longer than in complexes 1 and 1*. The shorter intermolecular Cr-Cr, Cr-Ni and Ni-Ni distances are 9.17, 6.84 and 8.56 Å respectively. This is due to p-p interaction and to hydrogen bonds between two free cyanides through a water molecule.

3. CrNi$_2$ complexes, magnetic behaviour
The magnetisation versus applied field was recorded on single crystals of the three CrNi$_2$ using an array of micro-SQUIDs [31]. Different from a classical SQUID magnetometer where the flux coupling between sample and SQUID is made by using a pick up coil, a micro-SQUID magnetometer allows a much better flux coupling since the sample is placed directly on the SQUID loops. The sensitivity achieved with our device is $10^{-17}$ emu, that is ten orders of magnitude better than a traditional SQUID magnetometer [32]. The sensitivity is smaller when the sample is much larger than the micro-SQUID. The high sensitivity of the magnetometer allows to study single crystals with dimensions from 10 to 500 µm. The magnetometer works in a temperature range between 0.035 and 10 K, in applied fields up to 1.4 T with sweeping rates as high as 1 T s$^{-1}$ and a field stability better than a microtesla. The field can be applied in any direction of the micro-SQUID plane by separately driving three orthogonal coils. In order to ensure a good thermalisation, the crystal is fixed by using Apiezon grease.

Here we report on the observation of canted ferromagnetic structure for the three different compounds of CrNi$_2$ with the same ground state spin 7/2. First we analyse the hysteresis loops of compound 1. Second, we correlate the structure with the magnetic behaviour. Third, we conclude with a comparison between the magnetisation data of the three crystals in order to establish if the intermolecular coupling is sensitive to small variations of the structure: terminal ligands or crystal symmetry.

We used the micro-SQUID to measure magnetisation hysteresis loops at different temperatures and different field sweep rates and also the magnetic susceptibility below 7 K. A single crystal was placed on the SQUID array with the (100) plane parallel to the SQUID plane. The hysteresis loops are independent on the field sweep rate,
suggesting that either resonant quantum tunnelling is hindered by intermolecular interactions or is much faster than the time scale of the micro-SQUID technique.

The magnetisation loops measured for different directions of the applied field in the (100) plane, proved that the magnetic behaviour is not isotropic in the plane. We have chosen two symmetry directions in the (100) plane which present distinct magnetic behaviour. The first direction is along the projection in the (100) plane of the bisecting line of two Ni - Cr - Ni molecular directions, showed to be an easy axis of magnetization. The second direction perpendicular to the first one, showed to be a hard axis of magnetization. The corresponding magnetizations versus applied field curves are presented in figure 2(a, b). In the first orientation (figure 2a), the magnetization is reversed from the negative saturation value to the positive saturation value in zero field. When increasing the temperature, the saturation magnetization decreases, but the zero field slope remains constant below 0.6 K. This is confirmed by the magnetic susceptibility measured in this direction (see figure 3a).

A fit to a Curie-Weiss law gives a positive Curie-Weiss constant of +0.6 K. Both results are typical of a system with ferromagnetic intermolecular coupling leading to long range ferromagnetic ordering. However, when the field is applied perpendicular to the easy axis of magnetization (second direction above), hysteresis loops (figure 2b) and susceptibility measurements (figure 3b) suggest an antiferromagnetic intermolecular coupling. This is established by the hysteresis loop shapes and the negative Curie-Weiss constant (-0.25 K).

The magnetic behaviour can be explained using the crystallographic structure. The CrNi$_2$ compound, 1, presents an uniaxal anisotropy with a small ferromagnetic exchange interaction between the molecules. The central chromium ions of the molecules define the (100) planes (figure 1), which are separated from each other by a water and halide layer (figure 4). There might be weak antiferromagnetic interactions via hydrogen bonds between the planes but that are not clearly established. There are two different orientations of the molecules centred in the same (100) plane. The angle between the two directions is 64°; the angle between each direction and (100) plane is 36°.

The magnetic moments have therefore two orientations corresponding to the two orientations of the molecules. The micro-SQUID magnetometer is sensitive only to the in plane component of the magnetization, in this case to the projected magnetisation into the (100) plane. The projection coupling of magnetic moments can be decomposed into two independent contributions: a net ferromagnetic coupling along the bisecting line of two moments and a net antiferromagnetic one perpendicular to this direction. The magnetization measured along the bisecting line of two moments (figure 5a) is sensitive only to the net ferromagnetic component (the antiferromagnetic one is perpendicular to the direction of magnetic field, that is insensitive to field variation). The two moments are reversed at the same time near zero field.

Perpendicular to the bisecting line (figure 5c) only the net antiferromagnetic component of the coupling is sensitive to the field variation (fig. 5c). For intermediate orientations (fig. 5b), the behaviour is a mixture of the two limiting cases.
FIG. 6: Hysteresis loops for the three samples 1, 1* and 3; the magnetic field is applied along the hard axis. The field amplitude of the antiferromagnetic plateau for compound 1* is lower than for compound 1 and higher than for compound 3 in agreement with the estimation of exchange interaction constant and with the fact that the molecules are closer in compound 1 than in compound 3. This points out the necessity to use bulkier ligands to reduce the intermolecular interaction. Other studies are in progress to better understand the correlation between the crystallographic structure and the magnetic behaviour in other directions of space.

4. Conclusions

The two different orientations of molecules in the crystals together with the intermolecular exchange interactions make CrNi$_2$ a model system for canted ferromagnetic structures. It is established that the intermolecular coupling is sensitive to small variations of the structure such as the crystal symmetry or the steric hindrance of the terminal ligand. Our study allows to better understanding the synthetic parameters that have to be tuned in order to minimise intermolecular exchange interactions, necessary condition to get single molecule magnets. The ligand, as well as the counter anions has to be as bulky as possible. To isolate the high spin molecules, it is also conceivable to dilute the molecules in a diamagnetic or a paramagnetic matrix. Preliminary results performed on the CrNi$_2$(tetren) compound co-crystallised in presence of CoNi$_2$(tetren) complex, viewed as an ordered paramagnetic medium indicate the validity of such a strategy, which is beyond the scope of the present communication.

[1] A. K. Powell, S. L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. del Giallo, F. Piralli, J. Am. Chem. Soc., 117, 2491 (1995).
[2] T. Mallah, C. Auberger, M. Verdaguer, P. Veillet, J. Chem. Soc., Chem. Commun. 61-62 (1995).
[3] Z. J. Zhong, H. Seino, Y. Mizobe, M. Hidai, A. Fujishima, S. Ohkoshi, K. Hashimoto, J. Am. Chem. Soc., 122, 2952-2953 (2000).
[4] M. Pilkington, S. Decurtins, Chimia, 54 n 10, 593-601 (2000).
[5] R. J. Parker, L. Spiccia, K. J. Berry, G. D. Sutton, B. Moubaraki, K. S. Murray, Chem Commun, 333 (2001).
[6] R. E. P. Winpenny, J. Chem. Soc., Dalton Trans., 1-10 (2002).
[7] S. M. J. Aubin, N. R. Dilley, M. B. Wemple, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. 120, 839 (1998).
[8] A. L. Barra, F. Bencini, A. Caneschi, D. Gatteschi, C. Paulsen, C. Sangregorio, R. Sessoli, L. Sorace, ChemPhysChem, 2, 523-531 (2001).
[9] W. Werndorfer, N. Alagna-Alcade, D. N Hendrickson, G. Christou, Nature, 416, 406-409 (2002).
[10] O. Kahn, Molecular Magnetism, Wiley-VCH, New York, (1993).
[11] Magnetism: Molecules to Materials, J.S. Miller and M. Drillon Editors, Wiley-VCH, Weinheim (2001).
[12] G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, MRS Bull., 25(11), 66-71 (2000) and references therein.
[13] D. N. Hendrickson et al., J. Am. Chem. Soc., 114, 2455-2471 (1992).
[14] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, Nature, 365, 141-143 (1993).
[15] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, J. Am. Chem. Soc., 115, 1804-1816 (1993).
[16] D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, Science, 265, 1054 (1994).
[17] S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou, D. N. Hendrickson, J. Am. Chem. Soc, 118, 7746-7754 (1996).
[18] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, Nature, 383, 145-147 (1996).
[19] L. Bokacheva, A. D. Kent, and M. A. Walters, Phys. Rev. Lett. 85, 4803 (2000).
[20] T. Lis, Acta Cryst. B, 36, 2042-2046 (1980).
[21] W. Wernsdorfer et al, Phys. Rev. Lett. 84, 12 (2000).
[22] A. Scuiller, T. Mallah, M. Verdaguer, A. Nivorozkhip, J.-L. Tholence, P. Veillet, New J. Chem. 20, 1-3 (1996).
[23] M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier dit Moulin, F. Villain, Coord. Chem. Rev. 190, 1023-1047 (1999).
[24] V. Marvaud, A. Scuiller, C. Decroix, J. Vaissermann, C. Guyard-Duhayon, F. Gonnet, M. Verdaguer, Chem. Eur. J. under press.
[25] V. Marvaud, C. Decroix, A. Scuiller, F. Tuyras, J. Vaissermann, C. Guyard-Duhayon, F. Gonnet, M. Verdaguer, Chem. Eur. J. under press.
[26] V. Marvaud, A. Scuiller, F. Tuyras, J. Vaissermann, C. Guyard-Duhayon, F. Fabrizi de Biani, M. Verdaguer, Chem. Eur. J. submitted to publication, (2002).
[27] V. Marvaud, M. Verdaguer et al. manuscript in preparation.
[28] A. Yamaguchi, N. Kusumi, H. Ishimoto, H. Mitamura, T. Goto, N. Mori, M. Nakano, K. Awaga, J. Yoo, D. N. Hendrickson, G. Christou, J. Phys. Soc. Jpn. 71, 2, 414-417 (2002).
[29] M. Affronte, J. C. Lasjaunias, W. Wernsdorfer, R. Sessoli, D. Gatteschi, S. L. Heath, A. Fort, A. Rettori, Phys. Rev. B 66, 064408 (2002).
[30] K. E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey, M. Verdaguer, J. Am. Chem. Soc. 122, 718-719 (2000).
[31] W. Wernsdorfer, Adv. Chem. Phys. 188, 99-190 (2001).
[32] M. Jamet, W. Wernsdorfer, C. Thirion, D. Mailly, V. Dupuis, P. Mlinon, A. Prez, Phys. Rev. Lett 86, 4676 (2001).