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Synthesis and characterization of [Cu(Me_2oxpn)Ni(NO_2)(tmen)](ClO_4): a single ferrimagnetic dinuclear Cu^{II}–Ni^{II} complex acting as weak molecule-based magnet

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The new heterodinuclear complex [Cu(Me_2oxpn)Ni(NO_2)(tmen)](ClO_4), that exhibits strong antiferromagnetic intramolecular coupling between Cu^{II} and Ni^{II} ions (ferrimagnetic behavior), shows ferromagnetic ordering at low temperature, due likely to a small canting phenomenon; it is one of the very few compounds made from isolated molecules that lead to cooperative magnetic behavior.

More and more researchers in coordination chemistry are interested by bulk magnetic properties.[1] One of the main challenges of this field is to design molecular-based compounds exhibiting spontaneous magnetization. Spectacular results have been reported in past years.[1,2] Additionally, molecules with high-spin multiplicity in the ground state have also been described.[3] To design molecular materials displaying zero-field magnetization below a critical temperature T_c one must assemble the magnetic molecular unit in such a way that the interaction between the local spin carriers at the scale of the lattice leads to a non-zero resulting spin. These results can be achieved, for example, by 3D-ferromagnetism, 3D-ferrimagnetism and, also, by the weak ferromagnetism derived from canted antiferromagnetic spins. If this is the case, a weak ferromagnetic transition is expected at T_c. Obviously, the onset of spontaneous magnetization results from a three-dimensional transition.[4] It is becoming evident that magnetic ordering is rather common in materials with extended structures but not in species formally derived from isolated molecules. Only very few examples have been reported: $\{K_2[CoO_3PCH_2N(CH_2COO)_2]_2\}_6{\cdot}xH_2O$,[5a] $[(Ni(bpm)_2)_3(Fe(CN)_6)_2]{\cdot}7H_2O$[5b] and some pure organic radicals.[6] Evidently, this kind of molecular entity must be linked by hydrogen bonds or van der Waals forces to give a three-dimensional network with magnetic ordering. Our strategy arises from using strong metal-ligand bonds and incorporates more flexible bonds between molecules. We have successfully used this synthetic strategy starting from ferrimagnetic molecules.[7]

We report here the synthesis of a new compound [Cu(Me_2oxpn)Ni(NO_2)(tmen)](ClO_4),† **1**, (Me_2oxpn = *N,N′*-bis(3,amino-2,2′-dimethylpropyl)oxamido; tmen = *N,N,N′N′*-tetramethylethylenediamine) which has been characterized by single-crystal X-ray structure analysis.‡ The drawing of the cationic part, with atom labeling scheme is given in Fig. 1(a). The Ni atom is in a distorted octahedral environment and the coordination polyhedron of Cu^{II} can be considered as a square-planar geometry. Its crystal structure is constituted by cationic $[Cu(Me_2oxpn)Ni(NO_2)(tmen)]^+$ and ClO_4^- anions giving supramolecular one-dimensional assemblies [Fig. 1(b)]. The chains show an alternation of [Cu–Ni] cation units linked by hydrogen bonds between the hydrogen atoms of the N(1) and the hydrogen atoms of the N(3) of the neighboring unit through oxygen atoms of the perchlorate ion. The [Cu–Ni] units are situated in a zigzag fashion along the chain.

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Susceptibility measurements for complex **1** are shown in Fig. 2(a) as χ_MT *vs.* T per Cu–Ni unit.§ From room temperature down to 40 K there is a clear fall in the χ_MT, which corresponds to the classical behavior for an isolated [Cu–Ni] entity coupled antiferromagnetically. **1** shows a clear decrease in χ_MT from 40 to 2 K. This decrease can be explained by magnetic interactions through hydrogen bonds, as described above. The fit was performed according to the Hamiltonian

$$H = -J\Sigma_{i=1}^{n/2}[S_{2i}S_{2i-1} + \alpha S_{2i}S_{2i+1}],$$

by irreducible tensor operator formalism (ITO) using the CLUMAG program.[8] The results were: J_1 (intra) = −115.0 cm^{-1}, J_2 (inter) = −2.16 cm^{-1}, g = 2.27 and R = 1.14 × 10^{-4}.

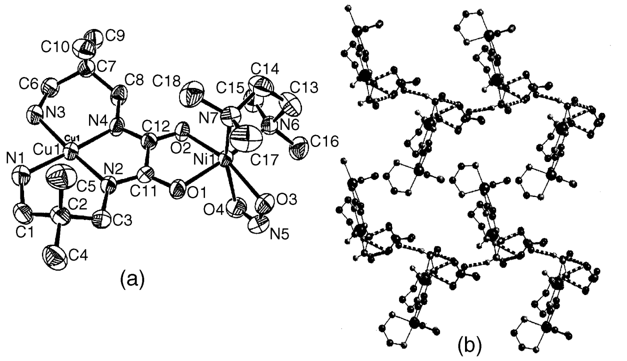

Fig. 1 (a) Drawing of the cationic part, with the atom labeling scheme of **1**. Ellipsoids at the 50% probability level. (b) Projection down the *zx* plane of the chains, showing the alternation of [Cu–Ni] cations linked by hydrogen bonds (dotted lines) through oxygen atoms of the perchlorate anion.

A closer examination of the magnetism of **1** revealed quite exceptional magnetic behavior for discrete magnetic molecules. The study of χ_MT *vs.* T at different fields, [Fig. 2(b)], shows a maximum in χ_MT at 11 K at lower fields. In a 100 G field, for instance, χ_MT rises to a maximum of 0.66 cm^3 K mol^{-1} and then falls rapidly as the temperature approaches 2 K. This transition at 11 K could indicate the onset of long-range magnetic ordering, although this phenomenon is not as abrupt as in other

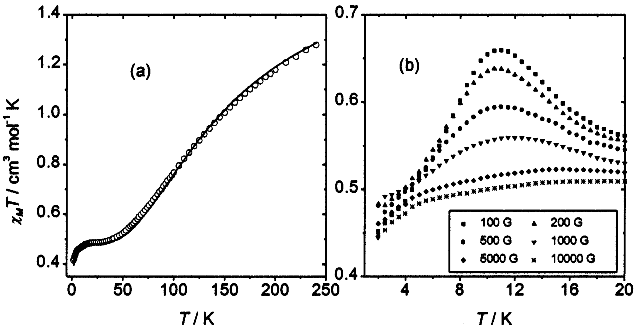

Fig. 2 (a) Experimental and calculated variations of the product χ_MT *vs.* T for **1** (10.000 gauss; at low fields there are cooperative phenomena, see (b); (b) temperature dependence of the product χ_MT *vs.* T for **1**, at the field values shown.

cases reported.[9] Further, to confirm the occurrence of magnetic phase transition, the DC magnetization was measured with the sample cooled in zero-field (ZFCM) and in a field of 100 gauss (FCM). The FCM gave a rapid increase below 15 K and the ZFCM diverged from FCM from about 11 K [Fig. 3(a)]. The difference ZFCM − FCM corresponds to the remnant magnetization (RM) induced on cooling within the field below *ca.* 11 K. This remnant magnetization is very weak (5 cm^3 G mol^{-1} at 2 K). At 2 K the magnetization curve exhibits a very small hysteresis cycle, with a coercive field of *ca.* 30 Oe (the possible error of the measurement is less than 10 Oe). Even very small, there is a remnant magnetization. In some few cases, these molecular-based magnets do not exhibit hysteresis, demonstrating weak anisotropy.[10] Finally, to complete the characterization of the magnetic ordering, the *ac* susceptibility measurements at 100 and 1000 Hz show an weak out-of-phase signal which has a maximum close to 11 K (the temperature of the onset of the magnetic ordering) [Fig. 3(b)].

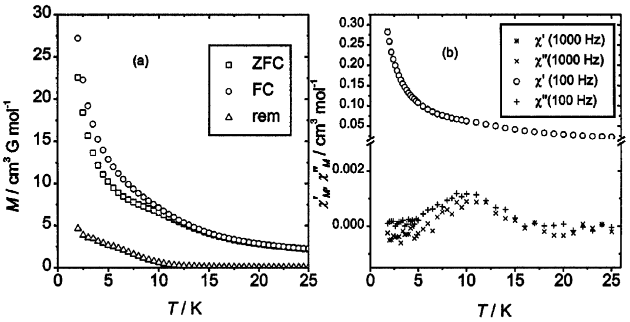

Fig. 3 (a) Temperature dependence of the magnetization, M, for **1** cooled in zero-field (ZFCM) and in field of 100 G (FCM). Remnant magnetization (RM) is also shown; (b) Real or in phase (χ') and imaginary or out-of-phase (χ'') components of the zero-field ac susceptibility (χ_{ac}) as a function of temperature, measured in an oscillating field of amplitude, H_{ac} = 3 G and frequencies, f = 100 and 1000 Hz.

The origin of this behavior, very rare for discrete molecules, should be emphasized that is due to the interactions between the molecules giving a three-dimensional net by hydrogen or van der Waals forces. Taking into account the strong intradinuclear antiferromagnetic coupling between Cu^{II} and Ni^{II} ($J = -115$ cm^{-1}) the ground state at 11 K, where the ferromagnetic ordering begins to be operative, is $S = \frac{1}{2}$. The phase change from paramagnet to ferromagnet could be due to a canted antiferromagnet indicating the significant influence of either the single-ion anisotropy or the antisymmetric part of the spin Hamiltonian, $\mathbf{d_{ij}}[S_i \times S_j]$.[11] In **1**, D and E are, in principle, zero because the ground state is $S = \frac{1}{2}$. The antisymmetric part is proportional to $[(g-2)/g]J$ where the intermolecular coupling, J, is -2.16 cm^{-1} and the average g value is 2.27 (which agrees with the value obtained by EPR). Thus, although small, this term is not zero. This is the reason given in the literature for Mn^{II} or even Cu^{II} canted complexes.[4c–e]

It is important to point out that we have also prepared and fully characterized the isostructural complex $[Cu(Me_2oxpn)Ni(NO_2)(trimen)](ClO_4)$ **2** (trimen = *N,N,N′*-trimethylethylenediamine), which does not show any signal of weak ferromagnetism (possible canted antiferromagnetism) neither in $\chi_M T$ values at different fields nor remnant magnetization or χ_M'' out-of-phase signal in ac susceptibility measurements. The only *apparent* difference between **1** and **2** is the presence of four methyl groups in the blocking amine of **1** (tmen) and three methyl groups in **2** (trimen). Thus, very fine subtleties could explain why complex **2** does not exhibit weak ferromagnetism, while complex **1**, does. Further studies are necessary to interpret the weak ferromagnetism in **1** and clarify the unexpected difference between the two isostructural complexes, **1** and **2**.

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Notes and references

† $[Cu(Me_2oxpn)Ni(NO_2)(tmen)](ClO_4)$ **1**: an ethanolic solution (20 mL) of *N,N,N′,N′*-tetramethylethylenediamine (tmen) (0.32 g, 2.73 mmol) was added to a stirred solution of $Ni(NO_3)_2 \cdot 6H_2O$ (1 g, 2.73 mmol) in ethanol (20 mL). A suspension of $[Cu(Me_2oxpn)]$[12] (0.87 g, 2.73 mmol) in ethanol (40 mL) was then added. The blue solution was filtered, and $NaNO_2$ (0.189 g, 2.73 mmol) was added. The resulting blue solution was left to evaporate slowly at room temperature. Violet monocrystals suitable for X-ray determination were collected after 1 week (yield *ca.* 65%) and were identified by IR spectroscopy and elemental analysis. Calc. (found): C, 33.70 (33.9); H, 6.30 (6.3); N, 15.31 (15.1)%.

‡ *Crystal data* for **1**: $C_{18}H_{40}ClCuN_7NiO_8$, crystal dimensions 0.45 × 0.40 × 0.35 mm, orthorhombic, space group *Pbca*, a = 11.616(1), b = 17.996(1), c = 26.613(1) Å, V = 5563.0(1) $Å^3$, Z = 8, D_c = 1.529 g cm^{-3}, T = 298 K, 36060 reflections, 6878 independent reflections (R_{int} = 0.0296). Lorentz polarization and absorption corrections were applied, μ = 1.590 mm^{-1}, 370 parameters refined, $R1$ = 0.0385, $wR2$ = 0.0936 (for all data). Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-87 computer program for crystal structure determination and refined by full-matrix least-squares methods on F^2, with the SHELXL-97 computer program. Hydrogen atoms were included in calculated positions and refined in riding mode. Ionic perchlorate shows high thermal parameters and less than ideal geometry.CCDC reference number 166398. See http://www.rsc.org/suppdata/cc/b1/b110747j/ for crystallographic data in CIF or other electronic format.

§ Magnetic susceptibility measurements were carried out on polycrystalline samples with a SQUID apparatus working in the range 2–300 K. To be sure of the magnetic measurements (magnetic ordering) the measurements have been performed in two different SQUIDS in two different Centers (Barcelona and Toulouse) with different samples. Results were concordant.

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