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Structural and Magnetic Characterization of a μ-1,5-Dicyanamide-Bridged Iron Basic Carboxylate $[Fe_3O(O_2C(CH_3)_3)_6]$ 1D Chain

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We are reporting an unprecedented example of a μ-1,5-dicyanamide (dca)-bridged iron basic carboxylate, $[Fe_3O(O_2C(CH_3)_3)_6]$, 1D chain. As revealed from X-ray determination, the Fe_3O cores are arranged in a zigzag configuration along the chain and strictly aligned in the same plane. The chains are well-isolated by the bulky *tert*-butyl groups. Magnetic measurements showed that the Fe_3O units are weakly antiferromagnetically coupled ($J = -0.6$ cm^{-1}) through the dca ligand while possessing a well-isolated $S = {}^1/_2$ spin ground state arising from competing antiferromagnetic interactions.

The preparation and study of molecular nanomagnets is currently one of the leading topics in the field of molecular magnetism.[1,2] Among these compounds, single-molecule magnets (SMMs) and single-chain magnets have received a great deal of attention because of their unique magnetic properties based on a slow relaxation of magnetization and their potential application in information storage and quantum computation at a molecular level.[3,4] Within this field, the assembly of preformed polymetallic clusters by covalent bonds in a step-by-step strategy has become a quite desired target for chemists.[3] As an example, the linking of SMM in a rational manner was introduced only some years ago.[5] Since then, this procedure has opened the way to 1−3D frameworks that exhibit properties ranging from classical to quantum magnetism.[2,6]

The "basic carboxylates", $[M_3O(O_2CR)_6]$ (with M a first-row d-block transition metal and R a suitable organic group) cores, known for decades,[7] are some of the most widespread moieties as starting reagents in the preparation of high-dimensional supramolecular arrangements, as for example,in the synthesis of the pioneer SMM, $Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4$.[8] In spite of this, there are only a couple of examples reported up to date where this μ_3-O core was used as a "true" building block for the construction of higher nuclearity clusters, specifically by linking them with appropriate bridging units through covalent bonds.[9] In only one of these cited cases, the synthetic approach relies on a rational linking of the preformed M_3O cores.

We have explored the reaction of the iron derivative, $[Fe_3O(O_2C(CH_3)_3)_6(H_2O)_3]^+$, with the potentially bridging dicyanamide (dca) monoanion, NC−N−CN. When the perchlorate salt of the iron complex[10] is mixed with a small excess of tetraphenylphosphonium dicyanamide in acetonitrile, a deep orange solution is obtained. Slow evaporation of the solvent afforded red crystals. Recrystallization from a dichloromethane/diethyl ether mixture afforded crystals suitable for X-ray diffraction. The structure determination reveals the presence of a 1D chain based on the stringing of the Fe_3O cores through the dca ligand in a 1,5-μ mode (Figures 1 and S3 in the Supporting Information), with formula $[Fe_3O(O_2C(CH_3)_3)_6(H_2O)(\mu\text{-1,5-dca})]_n$ (**1**).

In contrast, when the same reaction is performed in a methanol/water mixture, only a nonbridged dca-substituted Fe_3O trinuclear complex is obtained, with the central N atom of the ligand coordinating in an uncommon mode to the metal (Figure S1 in the Supporting Information).

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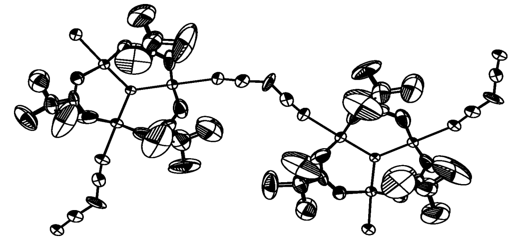

Figure 1. ORTEP drawing of the chain structure of compound **1**. H atoms were omitted for clarity. Ellipsoids probability: 50%.

The dicyanamide salt of the fully methanol-substituted complex cocrystallized, interacting through hydrogen bonds to give the general formula $[Fe_3O(O_2C(CH_3)_3)_6(CH_3OH)_3]dca\cdot[Fe_3O(O_2C(CH_3)_3)_6(CH_3OH)_2dca]$ (**2**; Figure S2 in the Supporting Information). These results suggest that avoiding O-donor solvents seems to be a key feature for obtaining the chain structure. When a noncoordinating solvent toward the Fe_3O core like CH_3CN is used, replacement of two of the coordinated waters by dca is observed, opening the way to the chain polymeric structure. This is not possible in methanol because of its strong bonding to the Fe_3O core.

The 1D chain complex **1** propagates along the *b* axis in a zigzag fashion, with alternating orientation of the triangular Fe_3O cores. The Fe_3O triangular cores belonging to the same chain are roughly held on the same $\overline{ab}$ plane, while all of the resulting "chain planes" are stacked parallel along the *c* axis, well-isolated from each other by means of the bulky carboxylate *tert*-butyl groups $[C(CH_3)_3]$. Chain−chain distances, measured between Fe_3O planes, are ca. 10 Å. Along the *a* axis, chains are well spaced by means of diethyl ether molecules contained in the crystal structure, with a distance measured from μ_3-O to μ_3-O of ca. 14 Å (Figure S4 in the Supporting Information). The trinuclear core $[Fe_3O(O_2C(CH_3)_3)_6]$ presents geometrical parameters, i.e., bond lengths and angles, similar to those of other related complexes.[11]

Surprisingly enough, this is just the second example of a structurally characterized $Fe^{III}-\mu$-1,5-dca$-Fe^{III}$ motif, with only the $Fe^{III}SB-\mu$-1,5-dca$-Fe^{III}SB$ (SB = Schiff base) complexes, which are also 1D chains, being known up to now.[12] The observed Fe−N distances of 2.113 and 2.118 Å are shorter than those observed in the mentioned $Fe^{III}SB$ compounds for which the Fe−N bond lengths range between 2.125 and 2.170 Å. It should be remarked that, with only a few exceptions, most of the observed Fe−N distances in Fe−dca complexes fall within this range.[13] Among the exceptions, a linear triazine-μ-oxodiiron(III) complex[14] is found where dca occurs as a terminal ligand. In this compound, both Fe−N bond lengths of 2.049 Å are extremely short. Complex **1** becomes the second example of a linear O−Fe−N_{dca} arrangement. The observed Fe−μ_3O distances opposing the N atoms of the dca ligand in complex **1** of 1.918 and 1.922 Å can be contrasted with the extremely short Fe−O distances observed in the above-mentioned complex of 1.763 Å. The remaining bond lengths of the dca ligand in complex **1** are in the range of the usually observed values.

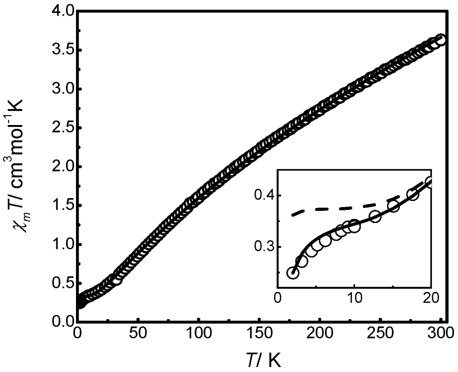

Figure 2. $\chi_m T$ vs T plot at 1 T of a powdered sample of complex **1**. Full line: best fitting with a Hamiltonian of eq 1 + mean-field correction. Inset: enlarged view of the low-T region. Full line: best fitting with a Hamiltonian of eq 1 + mean-field correction. Dashed line: best fitting above 15 K with the Hamiltonian of eq 1.

The nonbridging coordinated dca in complex **2** is a rare example because there are only a few known structurally characterized complexes of this type containing Co and Cu as metallic centers.[15,16] Hence, we report here on the first example containing Fe. The Fe−N distance is 2.165 Å, clearly larger than that observed in chain complex **1**.

IR spectra in the region 2100−2300 cm^{-1}, measured as KBr pellets, appear to be revealing. While the sodium salt of the dca anion shows three intense peaks at 2180, 2230, and 2290 cm^{-1} corresponding to the normal modes of the terminal CN stretching, complex **1** shows only a broad intense peak at 2180 cm^{-1} with a weaker peak at 2142 cm^{-1}. Most probably, the unique broad peak observed for complex **1** is reflecting the superposition of the several CN stretching modes along the chain. Other reported dca chains also show a diminution in the number of IR CN stretching peaks with respect to the free ligand.[16]

In order to gain insight into the magnetic properties of complex **1**, we performed direct current magnetization measurements in the temperature range 2−300 K (Figure 2) under an applied field of 1 T. The $\chi_m T$ value per Fe_3O moiety at 300 K is with 3.64 cm^3 K mol^{-1}, well below the expected value for three isolated high-spin Fe^{III} ions, 13.12 cm^3 K mol^{-1}, indicating strong antiferromagnetic interactions within the complex. When the temperature is decreased, $\chi_m T$ steadily decreases to reach a value of 0.4 cm^3 K mol^{-1} at 15 K, after which it continuously drops up to 2 K.

This behavior is typical for spin-frustrated systems with competing antiferromagnetic exchange interactions and was already observed for these Fe_3O "basic carboxylate" com-

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pounds.[7,17] In fact, the χ_mT vs T plot for complex **2** evidences a similar profile only differing in the low-temperature region.

We attempted a full fitting of the data by obtaining the energy of the different spin states and calculating the molar susceptibility for all possible field orientations (see details in the Supporting Information). In this case, the Heisenberg spin Hamiltonian describing the isotropic exchange interactions within an isosceles Fe3 triangle of C_2 symmetry (Fe$-\mu_3$O distances: 1.920, 1.921, and 1.874 Å) is given by eq 1:

$$H = -2J_a(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3) - 2J_b(\hat{S}_2 \cdot \hat{S}_3) \qquad (1)$$

Up to here, the interaction between the Fe_3O units along the chain mediated by the dca ligand is being neglected. This assumption appears quite sensible because the χ_mT vs T profile of **1** closely resembles the one for **2** (Figure S6 in the Supporting Information). Additionally, it has been observed that the dca ligand in its μ-1,5 mode only develops weak interactions, usually less than 1 cm^{-1}.[13] However, the magnetic behavior below 15 K cannot be satisfactorily reproduced with this model (inset in Figure 2). By correction of the molar susceptibility by a mean-field approximation[18] (see Supporting Information) to treat the dca-mediated intrachain Fe_3O core interaction, the experimental data are now well reproduced in the whole temperature range (Figure 2). Either with a Hamiltonian of eq 1 or with the additional mean-field correction, two reasonable calculated χ_mT plots from the mathematical point of view can be obtained as reflected by the error contour plot (Figure S7 in the Supporting Information). However, only one of them appears meaningful, the one with $|J_a| > |J_b|$, because the shorter exchange pathway Fe−O−Fe corresponds to the equivalent sides of the isosceles triangle. The best fitting parameters obtained with a Hamiltonian of eq 1 + mean-field correction are as follows: $J_a = -35.3 \pm 0.3$ cm^{-1}, $J_b = -28.3 \pm 0.3$ cm^{-1}, and $zJ = -1.3 \pm 0.2$ cm^{-1} ($R = 5.7 \times 10^{-5}$),[19] with g fixed at value of 2.0. Without considering the mean-field correction, above 15 K: $J_a = -36.9 \pm 0.2$ cm^{-1} and $J_b = -29.7 \pm 0.1$ cm^{-1} ($R = 8.9 \times 10^{-7}$) with again a fixed $g = 2.0$. The obtained values for J_a and J_b are comparable to other reported Fe_3O basic carboxylates, including compound **2**, for which we obtained with eq 1 $J_a = -30.7 \pm 0.1$ cm^{-1} and $J_b = -25.5 \pm 0.1$ cm^{-1} ($R = 3.7 \times 10^{-7}$) (Figure S7 in the Supporting Information). No fitting improvement is achieved for the χ_mT plot of complex **2** when including an intermolecular mean-field interaction term.

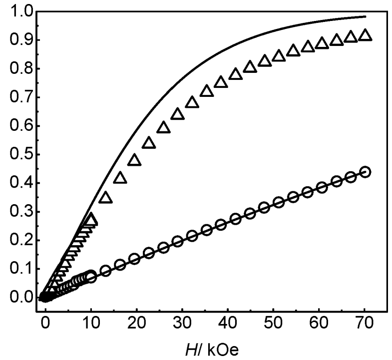

Figure 3. M vs H plot at 10 K (circles) and 2 K (triangles) of a powdered sample of complex **1**. Full line: calculated Brillouin function for $S = {}^1/_2$ and $g = 2.0$.

From the obtained exchange coupling constants for the chain complex **1**, a well-isolated (first $S = {}^1/_2$ excited state, 42 cm^{-1} above) ground-state spin, $S = {}^1/_2$, is expected. In fact, field dependence magnetization measurements performed at 10 K for complex **1** afforded an M vs H plot strictly following a Brillouin function for $S = {}^1/_2$ with a $g = 2.0$ value (Figure 3).

At 2 K, the experimental curve is somewhat below the expected Brillouin behavior, confirming the existence of weak intrachain antiferromagnetic interactions. In contrast, this is not observed for complex **2** (Figure S9 in the Supporting Information). Because z is well defined and equal to 2 for chain complex **1**, a value of J' of about -0.6 cm^{-1} is obtained for the interaction between Fe^{III} bridged by the dca ligand. As already mentioned, this value agrees with previously reported ones for bridging dca systems.[13]

The successful synthesis and structural characterization of complex **1** constitute an important step toward a rational synthetic strategy for linking preformed transition-metal clusters, preserving their identity. By a suitable choice of the reaction solvent, we have succeeded in stringing basic carboxylate Fe_3O cores with the bridging ligand dca. Additionally, magnetic measurements show that these μ_3-O moieties found in this 1D chain exhibit a well-isolated $S = {}^1/_2$ ground-state spin. It is worth adding that the presented result opens new possibilities to the design and construction of molecular-based magnetic materials.

Changes in the M_3O basic carboxylate as well as in the bridging ligand that we are currently exploring will be reported in the near future.

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Supporting Information Available: Crystallographic data in CIF format of **1** and **2** and all of the complementary information cited in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Error parameters within the 95% confidence interval. Agreement factor $R = 1/(N - n_p)[\Sigma(\chi_{calcd}T - \chi_{obsd}T)^2/\Sigma(\chi_{obsd}T)^2]^{1/2}$, where N is the number of experimental points and n_p is the number of parameters.