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First tetrameric Ni^{II} cluster with planar triangular topology exhibiting ferromagnetic pathways

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$[Ni_4L_3(H_2O)_2](ClO_4)_2{\cdot}2H_2O$ 1, the first tetranuclear Ni^{II} cluster showing triangle planar geometry, formed with a new carboxylic-functionalized 1,5-diazacyclooctane bridging ligand has been presented; the global magnetic coupling is ferromagnetic and anisotropic calculations have been made.

The rational design and synthesis of polynuclear coordination complexes, aiming at understanding the structural and chemical factors that govern the exchange coupling between paramagnetic centers, are of continuing interest in biology, chemistry and physics.[1] Particular interest has focused on the development of single molecular magnets and the smallest aggregates showing this behavior are tetranuclear systems.[2] Of the relatively small number of known tetranuclear Ni^{II} complexes, hemicubane,[3] butterfly (cubane),[4] square (rhomb),[5] dicubane[6] and chair[7]-like cores have been observed. A variety of ligands have been employed for preparation of the clusters with carboxylate being one of the most widely used versatile bridges. The work by Darensbourg *et al.* and our group[8,9] indicate that diazamesocyclic ligands, such as 1,5-diazacyclooctane (DACO), modified by suitable donor pendants could be good building blocks for construction of polynuclear complexes with unique structures and functions. Thus, we anticipated that the incorporation of the carboxylic groups on the backbone of DACO would lead to fascinating clusters when treated with metal ions. Here we report a ferromagnetic tetranuclear Ni^{II} complex with bis(3-propionyloxy)-1,5-diazacyclooctane (H_2L), $[Ni_4L_3(H_2O)_2](ClO_4)_2{\cdot}2H_2O$ **1**, the structure of which has a unique planar triangular Ni_4 topology.†

The crystal structure‡ of **1** indicates that it is spontaneously resolved as chiral crystals (space group C_2 with Flack parameter of zero, indicating each individual crystal consists of a single enantiomer);[10] exactly planar trigonal geometry is determined by a crystallographic 2-fold axis passing through Ni(1) and Ni(2) (Fig. 1). Carboxylato groups link the four Ni^{II} ions in a μ_3-fashion bridging Ni(1) and Ni(2)/Ni(3) (*syn-syn*) with O bound to Ni(3)/Ni(2), and in a monatomic μ-fashion bridging Ni(1) and Ni(3). The central Ni(1) is in a distorted octahedral coordination geometry and connected to the other three Ni^{II} ions by the monatomic bridges of six carboxylato groups. The Ni(1)–O(3A)–Ni(3A)–O(1A) moiety forms dihedral angles of 78.0 and 83.0° with the planes through Ni(1)–O(6)–Ni(2)–O(6A) and Ni(1)–O(3)–Ni(3)–O(1). Consequently, the Ni_4 motif has a propeller shape and is chiral. The vertex Ni^{II} ions are coordinated by DACO moieties of L with unusual chair/chair configurations[9] and by two additional carboxylato groups for Ni(2) and a H_2O for Ni(3). The carboxylato groups show two bridging modes to link the Ni^{II} ions with Ni···Ni distances of 2.940, 3.173, 4.873 and 6.111 Å for Ni(1)···Ni(2), Ni(1)···Ni(3), Ni(2)···Ni(3) and Ni(3)···Ni(3A). The Ni(2)–Ni(1)–Ni(3) and Ni(3)–Ni(1)–Ni(3A) angles are 105.6(2) and 148.7(2)°. The Ni–O–Ni angles of the monatomic bridging carboxylato groups are 99.9(1)° [Ni(1)–O(1)–Ni(3)], 89.9(1)° [Ni(1)–O(6)–Ni(2)] and 95.5(1)° [Ni(3)–O(3)–Ni(1)], respectively. In the crystal, the tetramers are well-isolated from each other with intermolecular contacts between the Ni^{II} ceters > 7 Å.

The exchange pathway connecting the Ni^{II} ions can be schematized as shown in Fig. 2. The Ni···Ni interactions between the spins $S = 1$ are transmitted through the oxo and carboxylato bridges. The magnetic behavior of **1** was measured on a SQUID susceptometer in the temperature range 2–300 K and the magnetic field range 0–5 T. The $\chi_M T$ value is 4.76 $cm^3\ mol^{-1}$ K at 300 K and increases with decreasing temperature (6.15 $cm^3\ mol^{-1}$ K at 8.5 K), then decreases down to a minimum value of 4.0 $cm^3\ mol^{-1}$ K at 2.03 K (Fig. 3). This curve suggests ferromagnetic coupling with the presence of a D (zero-field splitting) parameter for Ni^{II} ions and/or antiferromagnetic intermolecular interaction, being active at low temperature.

In some simple cases, calculations of the spin levels of this kind of cluster can be performed by Kambe's method,[11] which, however, is restricted to isotropic cases with high symmetry. To

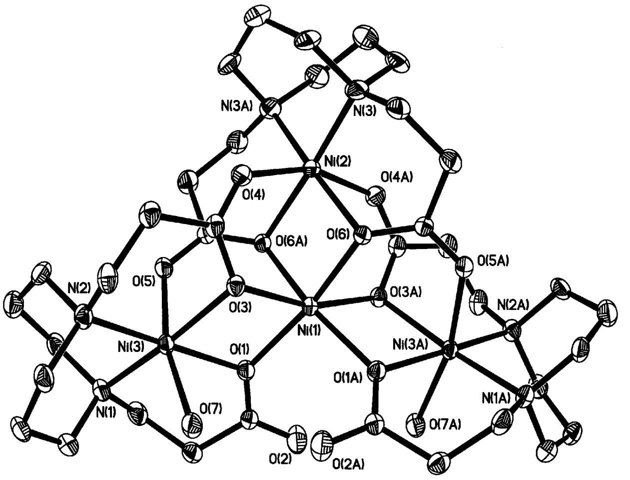

Fig. 1 ORTEP view of the $[Ni_4L_3(H_2O)_2]^{2+}$ cation with 30% probability ellipsoids (H atoms omitted for clarity).

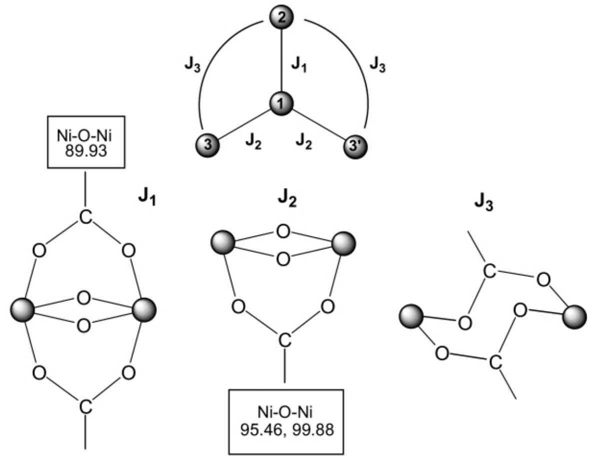

Fig. 2 Spin topology for **1** assuming different J values.

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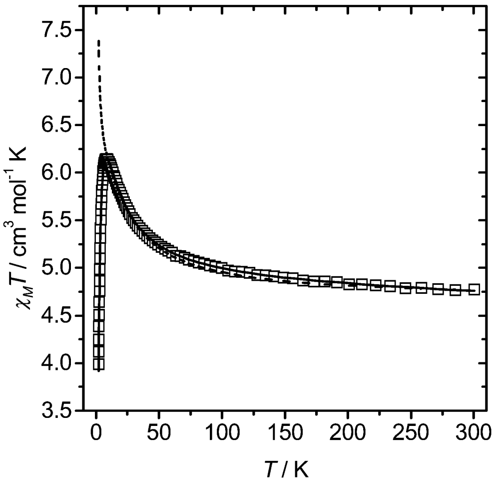

Fig. 3 A plot of $\chi_M T$ *vs.* T for **1**: the curve represents the best fit and the points the experimental data. The theoretical behavior of a fully isotropic ferromagnetic Ni_4 cluster is included as a dotted line.

consider the anisotropic terms of the electronic Hamiltonian, Clemente and coworkers have developed a general procedure (MAGPACK program).[12] The used Hamiltonian for **1** is $H = -2J_{ij}\Sigma S_iS_j + DS_{iz}^2$. Thus, a rigorous treatment has been carried out considering both isotropic exchange interactions and an axial single ion anisotropy of the type DS_{iz}^2. The best-fit parameters obtained with this computing model are: $J_1 = 5.12$ cm^{-1}, $J_2 = 0.35$ cm^{-1}, $J_3 = 0.23$ cm^{-1}, $D = 7.7$ cm^{-1}, $g = 2.17$ and $R = 1.05 \times 10^{-5}$. The TIP was assumed as 600×10^{-6} cm^3 mol^{-1}, a typical value reported in the literatures for Ni_4 compounds.[3,7,13] All J parameters seem to be logical, taking into account the symmetry and geometry of Ni^{II} ions: Ni–O–Ni angles lie close to 90° for J_1 and 95–100° for J_2, being in the range for Ni···Ni ferromagnetic exchange pathways to be dominant (90 ± 14).[14] The effect of the acetato bridge in *syn-syn* configuration is antiferromagnetic,[15] thus, it can mediate an additional exchange pathway and reduce significantly the ferromagnetic contribution. Coupling J_1 arises from a planar Ni–O–Ni–O fragment (Fig. 2) with Ni–O–Ni angles of 90° (the lowest reported so far). This angle will enhance the ferromagnetic coupling, but the presence of two carboxylato ligands (*syn-syn*) will reduce this coupling. On the other hand, J_2 arises from a non-planar Ni–O–Ni–O entity, with greater Ni–O–Ni angles, thus leading to low ferromagnetic coupling as observed that is further reduced by the presence of only one carboxylato group. Experimentally both contributions are quasi-balanced, giving a small positive J value. Coupling J_3 arises from the carboxylato group bridging two Ni^{II} fons in *syn-anti* mode, and gives rise to a low ferromagnetic contribution.[15]

From the J and D parameters it is not possible to calculate the ground state in the form of an S_T value. J_1 and D are of similar magnitude and J_2 and J_3 are very small. Thus, S is not a good quantum number to describe the ground state, but rather M_s. The calculations of the eigenvalues and eigenvectors from the MAGPACK program[12] gave a ground state of energy −44.63 cm^{-1} energy, with $M_s = 0$ with a contribution of 9 wavefunctions (of 81 possible) in which only 43% is due to the $S_T = 4$ contribution. There are also two contributions of approximately 20% due to two $S_T = 2$ states.

Finally, the presence of normally antiferromagnetic intermolecular interactions (J') is likely. When $J \gg J'$ it is possible to deduce this J' value applying the mean-field approximation,[16] although an empirical susceptibility formula is necessary. Therefore, the high experimental D value must be considered carefully because this J' parameter is also active at low temperatures. Although the D factor seems too great, it is of similar order of magnitude that those reported for Ni_2 and Ni_4 clusters (perfectly isolated), and exactly calculated with Inelastic Neutron Scattering (*ca.* 7 and 5 cm^{-1}).[17] A simple calculation with the same MAGPACK program was performed from room temperature to 15 K, to avoid the decreasing values of $\chi_M T$ at low temperatures. The best-fit parameters obtained with this computing model are: $J_1 = 5.53$ cm^{-1}, $J_2 = 0.25$ cm^{-1}, $J_3 = 0.22$ cm^{-1}, $g = 2.16$ and $R = 1.3 \times 10^{-5}$. The TIP was also assumed as 600×10^{-6} cm^3 mol^{-1}. These J values vary (*ca.* 10%) when cutting the experimental points at 15, 20, 25 or 30 K, respectively, indicating the importance of the D factor.

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Notes and references

† H_2L: to a solution of DACO·2HBr (10.7 mmol) and LiOH (24.5 mmol) in CH_3OH (30 mL) after stirring for 4 h was added a solution of 3-chloropropionic acid (33.5 mmol) and additional LiOH (32.4 mmol) in ethanol (20 mL) dropwise over 2 h under stirring. The mixture was then heated to reflux for 8 h at pH ~ 9. H_2L·2HCl was obtained as a white solid upon acidification (adjusted with 6 M HCl solution) and was recrystallized from H_2O–CH_3OH in 85% yield. Mp 192–194 °C. ^1H NMR (400 MHz, D_2O): δ 2.25–2.33 (m, 4 H), 2.81 (t, J 7.0 Hz, 4 H), 3.40–3.49 (m, 8 H).

1: Green block crystals were obtained in 75% yield by slow evaporation of an aqueous solution of $Ni(ClO_4)_2$·$6H_2O$ and H_2L·2HCl in 4 : 3 molar ratio by adjusting the pH to 5–6 with KOH. IR (KBr pellet, cm^{-1}): 1607vs $\nu_{as}(COO^-)$, 1389vs $\nu_s(COO^-)$, 1107vs and 625s $\nu(ClO_4^-)$. Anal. Calc. for **1**: C, 33.92; H, 5.38; N, 6.59. Found: C, 33.88; H, 5.57; N, 6.51%.

‡ *Crystal data* for **1**: $C_{36}H_{68}Cl_2Ni_4N_6O_{24}$, $M_r = 1274.70$, monoclinic, space group C_2, $a = 24.253(7)$, $b = 12.158(4)$, $c = 8.378(2)$ Å, $\beta = 98.557(4)°$, $V = 2443.0(12)$ Å^3, $F(000) = 1328$, $Z = 2$, $\mu = 1.718$ mm^{-1}, $D_c = 1.733$ g cm^{-3}, 5084 reflections measured, 3350 unique ($R_{int} = 0.0168$). Final R, wR and S values are 0.0329, 0.0878 and 1.053, respectively. CCDC reference number 167337. See http://www.rsc.org/suppdata/cc/b2/b203487p/ for crystallographic data in CIF or other electronic format.

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