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A Heterotetranuclear [$Ni^{II}Re^{IV}{}_3$] Single-Molecule Magnet

José Martínez-Lillo,[†] Donatella Armentano,[‡] Giovanni De Munno,*,[‡] Wolfgang Wernsdorfer,[§]
Miguel Julve,[†] Francesc Lloret,[†] and Juan Faus*,[†]

Departament de Química Inorgànica/Instituto de Ciencia Molecular, Facultat de Química de la Universitat de València, Avda. Dr. Moliner 50, 46100 Burjassot, València, Spain, Dipartimento di Chimica, Università della Calabria, via P. Bucci 14/c, 87030 Arcavacata di Rende, Cosenza, Italy, and Laboratoire Louis Néel-CNRS, BP166, 25 Avenue des Martyrs, 38042 Grenoble, Cedex 9, France

Received June 21, 2006; E-mail: demunno@unical.it; juan.faus@uv.es

Since the discovery of discrete species which can exhibit the phenomenon of single-molecule magnetism,[1] a large amount of work has been devoted to their preparation and characterization because of the need for knowledge of their fundamental properties [systems where exists an energy barrier to the relaxation of the magnetization which is due to the occurrence of a large ground spin state with a significant negative zero-field splitting (D)] and potential applications (molecular units for data storage and quantum computation).[2,3] The majority of the examples of single-molecule magnets (SMMs) concerns homometallic Mn polynuclear complexes where the anisotropy is created by the presence of Jahn−Teller distorted Mn^{III} ions. The need for a larger magnetic anisotropy, higher ground spin states and a better understanding of quantum tunneling effects through synergy of heterometal spins, moved preparative chemists toward the heterometallic SMMs as illustrated by recent reports on mixed 3d−4f complexes.[4]

In the context of our research activity in molecular magnetism, we have focused on the design stable mononuclear Re(IV) complexes and their use as ligands toward first row transition metal ions.[5] Re(IV) is a $5d^3$ ion which forms usually octahedral complexes that have two very important characteristics from a magnetic viewpoint: (i) a large degree of spin delocalization on the ligands in its complexes because of covalency effects,[6,7] and (ii) its remarkable magnetic anisotropy which is due to the high value of the spin−orbit coupling parameter (λ ca. 1000 cm^{-1} in the free ion).[5] These features together with the well-known capability of the oxalate (ox) ligand to transmit electronic interactions between the magnetic centers when acting as a bridge,[8] make the mononuclear complex $[ReCl_4(ox)]^{2-}$ a very suitable candidate for metal assembling in magneto-structural studies.

In this work we present the first example of a tetranuclear Ni^{II}-$Re^{IV}{}_3$ complex of formula $(NBu_4)_4[Ni\{ReCl_4(ox)\}_3]$ (**1**) which behaves as a SMM that is prepared by the reaction of nickel(II) nitrate hexahydrate and $(NBu_4)_2[ReCl_4(ox)]$ in nonaqueous solutions.

The structure of **1** consists of discrete tetranuclear $[Ni\{ReCl_4(ox)\}_3]^{4-}$ anions (Figure 1) and $[n\text{-}(C_4H_9)_4N]^+$ cations which are held together by electrostatic forces. Both metal atoms are six coordinated: six oxalate-oxygen atoms (at the Ni) and four chloro and two oxalate-oxygen atoms (at the Re) build somewhat distorted octahedral surroundings. The values of the Ni−O, Re−O, and Re−Cl bond lengths vary in the ranges 2.059(4)−2.095(4), 2.058(5)−2.097(4), and 2.283(3)−2.347(2) Å, respectively. The values of the bite angle subtended by the oxalate cover the ranges 79.2(2)−79.7(2)° (at the Re) and 81.6(2)−82.4(2)° (at the Ni). The values of the dihedral angles between the mean planes of the oxalate ligands are 88.4(1), 89.0(1), and 77.3(1)°. The degree of twist of the trischelated environment of the nickel atom is 49° (the twist angle ϕ is 60° for a regular octahedron).[9] The four metal atoms of the tetranuclear unit are coplanar and each polynuclear entity is well separated from each other (Figure S1) [the shortest intermolecular Re···Re and Cl···Cl separations being 9.803(1) and 5.608(3) Å, respectively]. The average Ni···Re distance across the bridging oxalate is 5.387(1) Å.

The magnetic properties of **1** under the form of $\chi_M T$ versus T plot (χ_M is the magnetic susceptibility per $Ni^{II}Re^{IV}{}_3$ unit) are shown in Figure 2. $\chi_M T$ at room temperature is 6.73 cm^3 mol^{-1} K, a value which is as expected for one nickel(II) ($S_{Ni} = 1$) and three rhenium(IV) ($S_{Re} = {}^3/_2$) ions magnetically isolated. Upon cooling, $\chi_M T$ continuously increases to reach a maximum value of 15.8 cm^3 mol^{-1} K at 6.0 K and further decreases to 14.4 cm^3 mol^{-1} K at 1.9 K. These features are typical of a significant intramolecular ferromagnetic interaction [a case of strict orthogonality between the interacting magnetic orbitals (t_{2g} vs e_g)] with a low-lying $S = 11/2$ spin state ($\chi_M T = 16.65$ cm^3 mol^{-1} K for $g_{11/2} = 1.93$).[10] The small decrease of $\chi_M T$ at very low temperatures is most likely due to zero-field splitting effects. The magnetic data were fitted through the Hamiltonian of eq (1) where the first term is the isotropic exchange interaction

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_{exchange} + \hat{\mathbf{H}}_{ZFS} + \hat{\mathbf{H}}_{Zeeman}$$

$$\hat{\mathbf{H}}_{exchange} = -J_{ReNi}\hat{S}_{Ni}\sum_{i=\mathbf{1}}^{\mathbf{3}}\hat{S}_{Rei}$$

$$\hat{\mathbf{H}}_{ZFS} = D_{Re}\Big[\sum_{i=\mathbf{1}}^{\mathbf{3}}\hat{S}_{ZRei}^{\mathbf{2}} - \mathbf{15/4}\Big] + D_{Ni}\Big[\hat{S}_{ZNi}{}^{\mathbf{2}} - \mathbf{2/3}\Big]$$

$$\hat{\mathbf{H}}_{Zeeman} = g_{Re}^{\parallel}\beta H\sum_{i=\mathbf{1}}^{\mathbf{3}}\hat{S}_{ZRei} + g_{Ni}^{\parallel}\beta H\hat{S}_{ZNi} + g_{Re}^{\perp}\beta H \Big[\sum_{i=\mathbf{1}}^{\mathbf{3}}\hat{S}_{XRei} + \sum_{i=\mathbf{1}}^{\mathbf{3}}\hat{S}_{YRei}\Big] + g_{Ni}^{\perp}\beta H(\hat{S}_{XNi} + \hat{S}_{YNi}) \quad (1)$$

between the Re^{IV} and Ni^{II} ions, the second one is the zero-field splitting of the interacting cations, and the last term accounts for the Zeeman effects. In order to avoid overparametrization, we assumed that all the rhenium centers are equivalent and $g_{\parallel} = g_{\perp}$ for both Re^{IV} and Ni^{II} ions. Given the strong correlation observed in the fitting procedure between the D_{Re} and D_{Ni} parameters, we made $D_{Ni} = 0$. The values of the best-fit parameters were $J = +16.3(3)$ cm^{-1}, $g_{Ni} = 2.18(1)$, $g_{Re} = 1.87(1)$, and $|D_{Re}| = 2.8(2)$ cm^{-1}. Assuming that the local D tensors are collinear, a value of $D_{11/2} = 0.46$ cm^{-1} is calculated through the expression $D_{11/2} = 0.163$ D_{Re}

[†] Universitat de València.
[‡] Università degli Studi della Calabria.
[§] Laboratoire Louis Néel-CNRS.

10.1021/ja0643873 CCC: $33.50 © 2006 American Chemical Society

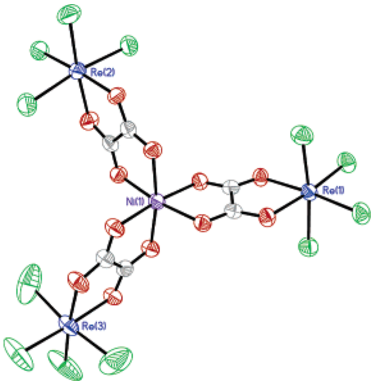

Figure 1. ORTEP drawing of the tetranuclear $[Ni\{ReCl_4(ox)\}_3]^{4-}$ anion of **1** with thermal ellipsoids at the 30% probability level.

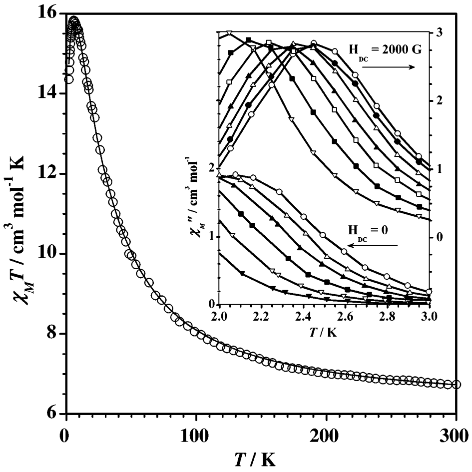

Figure 2. Thermal variation of the $\chi_M T$ product for **1** under an applied magnetic field of 100 G: (o) experimental data; (—) best-fit curve (see text). The inset shows the frequency and temperature dependence of the out-of-phase ac signal under external applied dc magnetic fields of 2000 (top) and 0 G (bottom) in a 1 G oscillating field and in the frequency range 100−1400 Hz.

$+ 0.0182\ D_{Ni}$. These results show that the only populated spin state at low temperatures is the $S = 11/2$ ground spin state. The small value computed for D_{Re} contrasts with the greater one for this parameter in the mononuclear $[ReCl_4(ox)]^{2-}$ anion.[5] A non collinear situation of the local D tensors in **1** would account for this difference. The computed value of $D_{11/2}$ agrees with that extracted from the magnetization plot at 2.0 K ($D_{11/2} = -0.50(5)$ cm^{-1}, Figure S2)

Frequency dependent out-of-phase ac signals are observed [inset of Figure 2 and Figure S3 (left)] which are indicative of a system with slow relaxation of the magnetization. For $H = 0$, no maxima of χ''_M are observed above 1.9 K in the frequency range explored. However, maxima of χ''_M are observed at $T > 1.9$ K for $H = 500$, 1000, and 2000 G, their position being shifted to greater temperatures with the increasing field. The data obtained were fit to the Arrhenius equation to give values of τ_0 (preexponential factor) and E_a (energy barrier) of 8.5×10^{-9} s and 16.2 cm^{-1} ($H = 2000$ G), 2.3×10^{-9} s and 14.2 cm^{-1} ($H = 1000$ G), and 2.9×10^{-8} s and 13.2 cm^{-1} ($H = 500$ G) (Figure S3, right). By extrapolation from these data, one can see that the value of τ_0 for $H = 0$ G must be close to 3×10^{-8} s. Also the linear field dependence of the energy barrier $E_a = U^\# + MH$ occurs with $M = 0.002$ cm^{-1} G which leads to $U^\# = 12.2$ cm^{-1} for $H = 0$ G [Figure S3, right (bottom)]. As in the present case $U^\# = D_{11/2}(S^2 - {}^1/_4)$ with $S = 11/2$, a value of 0.41 cm^{-1} is derived for $D_{11/2}$ in agreement with the value obtained for this parameter through the above fit of the $\chi_M T$ data.

In order to investigate possible SMM behavior, single-crystal magnetization measurements were performed with an array of micro-SQUIDS at temperatures down to 40 mK. Hysteresis loops for **1** at varying temperatures and sweep rates are shown in Figure S4. These curves show that an extremely fast tunneling occurs at zero applied field. However, when a field is applied the tunneling is switched off and sweep rate and temperature-dependent hysteresis loops occur, a behavior which was previously observed in cyano-bridged heterometallic species.[11]

In summary, **1** is best described as either a SMM with a fast tunnel transition at $H = 0$ G or as a compound whose SMM behavior is only "switched-on" by the application of an external magnetic field.

Acknowledgment. This research was supported by the Italian MIUR, the Spanish MEC (Project CTQU2004-03633) and the EU (Project QueMolNa MRTN-CT-2003-504880).

Supporting Information Available: Figures S1−S4, experimental details, and the CIF file of **1.** This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0643873