A High-Nuclearity 3d/4f Metal Oxime Cluster: An Unusual Ni$_8$Dy$_8$ “Core—Shell” Complex from the Use of 2-Pyridinealdoxime

Constantina Papapantiatifalloyopoulos,† Theocaris C. Stamatas,‡ Constantin G. Efthymiou,‡ Luis Cunha-Silva,§§ Filipa A. Almeida Paz,§ Spyros P. Perlepes,*,‡ and George Christou*,†

†Department of Chemistry, University of Florida, Gainesville, Florida, 32611-7200, ‡Department of Chemistry, University of Patras, 265 04 Patras, Greece, §§REQUIMTE and Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal, ¶Centro de Química Estrutural, Instituto Superior Técnico, Technical University of Lisbon, 1049-001 Lisbon, Portugal, and *CICECO and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

Received August 4, 2010

The initial employment of 2-pyridinealdoxime in 3d/4f chemistry has led to a Ni$_8$Dy$_8$ cluster with an unprecedented metal topology; the compound has an unusual structure, is the highest-nuclearity metal oxime cluster to date, and exhibits slow magnetization relaxation.

Large $D$ value, will lead to 3d/4f SMMs with properties significantly different from those of homometallic 3d ones. Indeed, this approach has successfully led to several Mn/Ln, Fe/Ln, Co/Ln, Ni/Ln, and Cu/Ln SMMs, with the majority of them being Mn/Ln species containing some Mn$^{III}$ centers. For such reasons, we are targeting new synthetic routes that might yield small-12a,b or large-nuclearity7a 3d/4f clusters.

From a synthetic viewpoint, methods must be devised to combine 3d and 4f ions within a cluster. One of our preferred routes is a “one-pot” procedure involving a mixture of 3d and 4f metal salts and a ligand possessing distinct functionalities for preferential binding of the 3d and 4f ions. The various anionic 2-pyridylmonoximes have been widely employed to date in the synthesis of structurally and magnetically interesting 3d and mixed 3d/3d metal complexes, but there is only one report of their use in low-nuclearity 3d/4f chemistry. These ligands are, in fact, particularly attractive for 3d/4f chemistry when the 3d metal is divalent because the deprotonated O atom will then favor binding to oxophilic Ln$^{III}$ ions, whereas the softer N atoms will favor the 3d M$^{III}$ atom. In the present work, we have thus employed 2-pyridinealdoxime (paoH), the simplest 2-pyridyloxime, in Ni/Ln chemistry; this had been used previously to prepare homometallic Ni$^{III}$ clusters14 but not for mixed 3d/4f chemistry. We

mixed-metal materials are a major research area for many groups around the world in the fields of solid-state chemistry and condensed-matter physics.1,2 Molecular chemists have also developed an intense interest in mixed-metal complexes during the last 2 decades. One reason for this is the search for compounds with interesting magnetic properties, such as single-molecule magnets (SMMs),3 single-chain magnets,4 and 3D molecular-based magnets.5 Polynuclear 3d/4f complexes occupy a special place among mixed-metal molecular materials because they offer an alternative6 to homometallic transition-metal SMMs. The hope has been that a lanthanide’s (Ln) often significant spin and/or its often large anisotropy, as reflected in a significant change in the magnetic properties upon application of an external magnetic field, will lead to SMMs with properties significantly different from those of homometallic 3d ones. Indeed, this approach has successfully led to several Mn/Ln, Fe/Ln, Co/Ln, Ni/Ln, and Cu/Ln SMMs, with the majority of them being Mn/Ln species containing some Mn$^{III}$ centers. For such reasons, we are targeting new synthetic routes that might yield small-12a,b or large-nuclearity7a 3d/4f clusters.

From a synthetic viewpoint, methods must be devised to combine 3d and 4f ions within a cluster. One of our preferred routes is a “one-pot” procedure involving a mixture of 3d and 4f metal salts and a ligand possessing distinct functionalities for preferential binding of the 3d and 4f ions. The various anionic 2-pyridylmonoximes have been widely employed to date in the synthesis of structurally and magnetically interesting 3d and mixed 3d/3d metal complexes,13b but there is only one report of their use in low-nuclearity 3d/4f chemistry.13c These ligands are, in fact, particularly attractive for 3d/4f chemistry when the 3d metal is divalent because the deprotonated O atom will then favor binding to oxophilic Ln$^{III}$ ions, whereas the softer N atoms will favor the 3d M$^{III}$ atom. In the present work, we have thus employed 2-pyridinealdoxime (paoH), the simplest 2-pyridyloxime, in Ni/Ln chemistry; this had been used previously to prepare homometallic Ni$^{III}$ clusters but not for mixed 3d/4f chemistry. We
have now discovered a synthetic route into an unusual $\text{Ni}_8\text{Dy}_8$ cluster, which also possesses interesting magnetic properties. We believe this work presages a rich new area of high-nuclearity 3d/4f metal oxime cluster chemistry.

The reaction of $\text{Ni(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Dy(NO}_3)_3 \cdot 6\text{H}_2\text{O}$, paoH, and NaOMe in a 1:1:3:3 molar ratio in MeOH led to a red solution, from which at room temperature slowly grew red crystals of $[\text{Ni}_8\text{Dy}_8\text{O(OH)}_4\text{(pao)}_2]^6^+\cdot \text{MeOH}_3\cdot \text{H}_2\text{O}$ (Figure 1) as 1:1 xMeOH:yH$_2$O (x > 7.5, y > 5) in 60% yield (based on available paoH). The complex crystallizes in monoclinic space group $P2_1/c$ with two independent $[\text{Ni}_8\text{Dy}_8\text{O(OH)}_4\text{(pao)}_2]^6^+$ cations in the asymmetric unit, but these are structurally very similar, and therefore only one will be discussed. The cation consists of eight octahedral Ni$^{II}$ and eight 8-coordinate Dy$^{III}$ atoms, held together by 1 $\mu_4$-O$^2^-$, 4 $\mu_3$-OH$^-$, and 28 pao$^-$ groups; the latter comprise 16 $\eta^1\eta^1\eta^2\mu_3$ (type A), and 4 $\eta^1\eta^1\eta^2\mu_3$ (type B) binding modes (Chart 1). There are no terminal ligands. The 16 metal atoms are arranged in an interesting topology: there is an inner Dy$^8$ core and an outer Ni$^8$ shell, linked through 16 diatomic oximate bridges (Figure 2, top). The Dy$^8$ core comprises a central $[\text{Dy}_4(\mu_4\text{O})_4]$ tetrahedron (Dy1, Dy2, Dy4, and Dy7), four of whose edges are each fused with an edge of a $[\text{Dy}_3(\mu_3\text{OH})_3]$ triangular unit. The resulting $[\text{Dy}_8(\mu_4\text{O}_4\text{(OH)}_4)]^{18^+}$ core is unique in Ln$^{III}$ chemistry (Figure 2, bottom). Protonation levels of O$^2^-$ and OH$^-$ ions were confirmed by oxygen bond-valence-sum calculations. The central $\mu_4$-O$^2^-$ ion is distorted tetrahedral [Dy–O–Dy = 103.8(3)–114.8(2)$^\circ$], and the tetrahedral $[\text{Dy}_3(\mu_3\text{OH})_3]$ triangular units are essentially isosceles, with the short separations [3.715(1)–3.735(1) Å] being the four (oxide)-(hydroxide)-bridged edges fused with the central tetrahedron. The remaining two edges of the central Dy$_4$ tetrahedron (Dy1Dy2 and Dy4Dy7) are each bridged by two $\mu$-O$^-$ atoms from two $\eta^1\eta^1\eta^2\mu_3$ (type B) pao$^-$ ligands. In addition, each


(15) Crystal structure data for 1: xMeOH:yH$_2$O: C$_{272}$H$_{368}$Ni$_{16}$Dy$_{16}$N$_{114}$O$_{38}$Cl$_{10}$, $F_w$ = 12269.45, monoclinic, space group $P2_1/c$ with $a = 21.973(2)$ Å, $b = 33.018(2)$ Å, $c = 64.448(5)$ Å, $\beta = 92.8(2)^\circ$, $V = 46700(6)$ Å$^3$, $T = 150(2)$ K, $Z = 4$, $R1[I > 2\sigma(I)] = 0.0818$, wR2($F^2$, all data) = 0.2350.

Dy\textsuperscript{III} of the tetrahedron is linked to two peripheral Dy\textsuperscript{III} by $\mu$-O\textsuperscript{−} atoms from two $\eta^1: \eta^1: \eta^2$ μ\textsubscript{3} (type A) pao\textsuperscript{−} ligands. The Dy···Dy and Dy···O distances are in the ranges 3.547(1)−3.805(4) and 2.075(1)−2.789(9) Å, respectively. If the bridging diatomic oximates are considered part of the inner Dy\textsubscript{8} core, then the latter is [Dy\textsubscript{8}(μ\textsubscript{4−}O)(μ\textsubscript{3−}OH)\textsubscript{6}(μ\textsubscript{3−}ONR)\textsubscript{4}−(μ-ONR)]\textsubscript{6}\textsuperscript{6+} (RNO\textsuperscript{−}, R = pao\textsuperscript{−}; Figure S1 in the Supporting Information).

The outer Ni\textsubscript{8} shell has a nonplanar square-based topology that can be described as comprising a Ni\textsubscript{4} square [Ni\textsubscript{4} ... Ni\textsubscript{5} ... Ni\textsubscript{7} ... Ni\textsubscript{8} ... Ni\textsubscript{4} are 11.623(8), 11.637(3), 11.641(6), and 11.570(2) Å, respectively; Ni ... Ni ... Ni ... Ni angles are in the 89.0−89.5° range] and a concentric Ni\textsubscript{4} tetrahedron [Ni ... Ni ... Ni ... Ni ... Ni angles in the 9.572(1)−10.992(1) Å and 54.8−69.4° ranges, respectively; Figure 2, top]. The Ni atoms of the tetrahedron thus alternate between lying above and below the Ni\textsubscript{4} square, giving approximately $\delta$\textsubscript{4} symmetry for the Ni\textsubscript{8} loop. The chromophores of the Ni\textsuperscript{III} atoms are all Ni\textsuperscript{II}Ni\textsubscript{6}. The outer Ni\textsubscript{8} is linked to the inner Dy\textsubscript{8} through 16 $\mu$-NO\textsuperscript{−} groups from the $\eta^1: \eta^1: \eta^2$ μ\textsubscript{3} pao\textsuperscript{−} ligands and through 8 $\mu$-μ\textsubscript{3}NO\textsuperscript{−} groups from the $\eta^1: \eta^1: \eta^2$ μ\textsubscript{3} (type A) ligands. Thus, the complete “core−shell” aggregate becomes [Ni\textsubscript{8}Dy\textsubscript{8}(μ\textsubscript{3}−O)(μ\textsubscript{3}−OH)\textsubscript{4}(μ\textsubscript{3}−ONR)\textsubscript{4}−(μ-ONR)]\textsubscript{6}\textsuperscript{6+} (Figure S2 in the Supporting Information). The voids between the cations are occupied by counterions and lattice solvate molecules; the crystal structure is stabilized by hydrogen bonds and intercationic $\pi$−$\pi$ interactions.

Complex 1 is the largest metal oxime cluster prepared to date, as well as the first Ni\textsubscript{8}Ln\textsubscript{8} complex and the first 3d/4f complex containing paoH. It is also one of the largest Ni/Ln clusters prepared to date, with only four examples at higher nuclearities, Ni\textsubscript{54}Gd\textsubscript{54},\textsuperscript{17} Ni\textsubscript{30}La\textsubscript{20},\textsuperscript{18} and Ni\textsubscript{21}Ln\textsubscript{20} (Ln = Pr, Nd).\textsuperscript{18}

Solid-state direct-current (dc) magnetic susceptibility ($\chi_M$) data on dried 1·4H\textsubscript{2}O were collected in the 5.0−300 K range in an applied field of 7 T and are plotted as $\chi_M$ vs $T$ in Figure 3. The $\chi_M$ vs $T$ value at 300 K is 128.5 cm\textsuperscript{3} K mol\textsuperscript{−1}. Essentially equal to the calculated 123.0 cm\textsuperscript{3} K mol\textsuperscript{−1} for eight Ni\textsuperscript{II} (S = 1/2) and eight Dy\textsuperscript{III} (6H\textsubscript{15/2} free ion; $S = \frac{5}{2}$; $L = 5$; $g_L = 4.3$) noninteracting ions. It slowly decreases with decreasing temperature down to ~100 K and then rapidly falls to 83.4 cm\textsuperscript{3} K mol\textsuperscript{−1} at 5.0 K because of a combination of depopulation of the Stark sublevels of the Dy\textsuperscript{III} 6H\textsubscript{15/2} state and Ni\textsuperscript{II}····Ni\textsuperscript{II} antiferromagnetic interactions. The $\chi_M$ T value at 5.0 K and the alternating-current (ac) in-phase $\chi_M$ vs $T$ value (Figure S4 in the Supporting Information) of ~55 cm\textsuperscript{3} K mol\textsuperscript{−1} at 1.8 K indicate significant remaining paramagnetism at the lowest temperatures. The large paramagnetism at 1.8 K and the considerable

---


---

Figure 3. $\chi_M$ vs $T$ data for 1·4H\textsubscript{2}O in a 0.1 T dc field. (inset) Out-of-phase $\chi''_M$ vs $T$ ac susceptibility signals in a 3.5 G field oscillating at the indicated frequencies.

In conclusion, the initial use of the versatile paoH group, the most flexible of the 2-pyridyloximes, in 3d/4f chemistry has led to the biggest metal oxime cluster to date and one that has an unusual “core−shell” segregation of its inner Dy\textsubscript{8} and outer Ni\textsubscript{8} units. This result shows that this ligand can indeed lead to high-nuclearity transition metal/lanthanide products with beautiful structures and interesting magnetic properties and without requiring the copresence of ancillary organic groups. We are currently targeting the Ni\textsubscript{8}Y\textsubscript{8} and Ni\textsubscript{8}Gd\textsubscript{8} analogues of 1 to provide a deeper insight into the nature of the intramolecular exchange interactions. This prototype product also suggests that employment of paoH promises to deliver many new and interesting Mn/Ln, Fe/Ln, Co/Ln, and Cu/Ln molecular species.

Acknowledgment. This work was supported by NSF Grant CHE-0910472 to G.C.

Supporting Information Available: Crystallographic data (CIF format) and other crystallographic details, the synthetic procedure and microanalyses, and structural (Figures S1 and S2) and magnetic (Figures S3−S5) plots for 1. This material is available free of charge via the Internet at http://pubs.acs.org.