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A High-Nuclearity 3d/4f Metal Oxime Cluster: An Unusual Ni_8Dy_8 "Core−Shell" Complex from the Use of 2-Pyridinealdoxime

Constantina Papatriantafyllopoulou,[†] Theocharis C. Stamatatos,[†] Constantinos G. Efthymiou,[‡] Luis Cunha-Silva,[§,⊥] Filipe 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*

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The initial employment of 2-pyridinealdoxime in 3d/4f chemistry has led to a $Ni^{II}_8Dy^{III}_8$ 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.

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 molecule-based magnets.[5] Polynuclear 3d/4f complexes occupy a special place among mixed-metal molecular materials because they offer an alternative[6] 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 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,[7] Fe/Ln,[8] Co/Ln,[9] Ni/Ln,[10] and Cu/Ln[11] 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-nuclearity[7a] 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,[13a,b] 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 hard, deprotonated O atom will then favor binding to oxophilic Ln^{III} ions, whereas the softer N atoms will favor the 3d M^{II} 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 clusters[14] but not for mixed 3d/4f chemistry. We

*To whom correspondence should be addressed. E-mail: perlepes@patreas.upatras.gr (S.P.P.), christou@chem.ufl.edu (G.C.).

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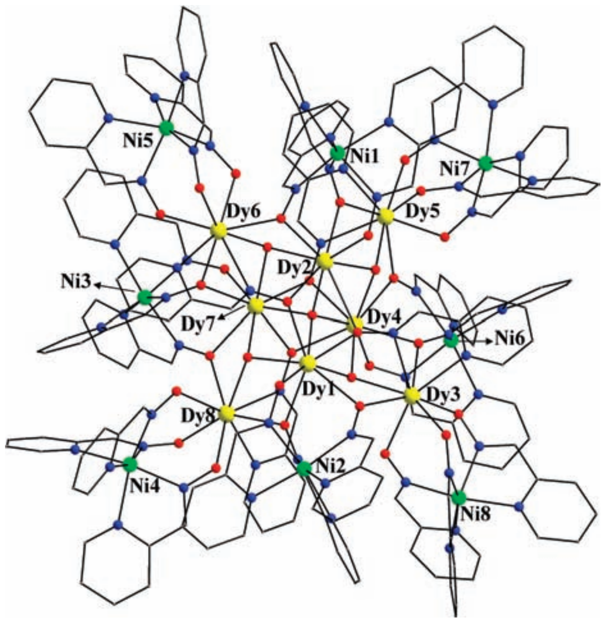
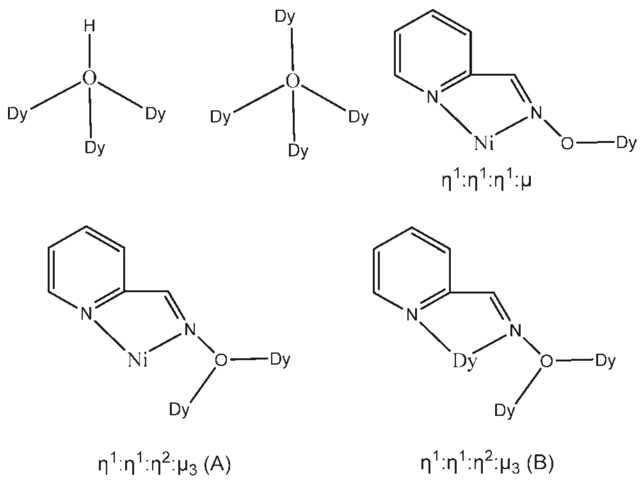


Figure 1. Partially labeled structure of one of the two crystallographically independent cations in **1**. Color scheme: Ni^{II}, green; Dy^{III}, yellow; O, red; N, blue; C, gray.

Chart 1. Crystallographically Established Coordination Modes of the Ligands Present in Complex **1**



have now discovered a synthetic route into an unusual Ni_8Dy_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 $Ni(ClO_4)_2 \cdot 6H_2O$, $Dy(NO_3)_3 \cdot 6H_2O$, 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 $[Ni_8Dy_8O(OH)_4(pao)_{28}](ClO_4)_5(NO_3)$ (**1**; Figure 1) as $\mathbf{1}\cdot x$MeOH$\cdot y H_2O$ ($x > 7.5$, $y > 5$) in 60% yield (based on available paoH). The complex crystallizes[15] in monoclinic space group $P2_1/c$ with two independent $[Ni_8Dy_8O(OH)_4(pao)_{28}]^{6+}$ 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 μ_4-O^{2-}, 4 μ_3-OH^-, and 28 pao^- groups; the latter comprise 16 η^1:η^1:η^1:μ, 8 η^1:η^1:η^2:μ_3 (type A), and 4 η^1:η^1:η^2:μ_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 $[Dy_4(\mu_4\text{-}O^{2-})]$ tetrahedron (Dy1, Dy2, Dy4, and Dy7), four of whose edges are each fused with an edge of a $[Dy_3(\mu_3\text{-}OH^-)]$ triangular unit. The resulting $[Dy_8(\mu_4\text{-}O^{2-})(\mu_3\text{-}OH^-)_4]^{18+}$ 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.[16] The central μ_4-O^{2-} ion is distorted tetrahedral [Dy−O−Dy = 103.8(3)−114.8(2)°], and the $[Dy_3(\mu_3\text{-}OH^-)]$ 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 μ-O^- atoms from two η^1:η^1:η^2:μ_3 (type B) pao^- ligands. In addition, each

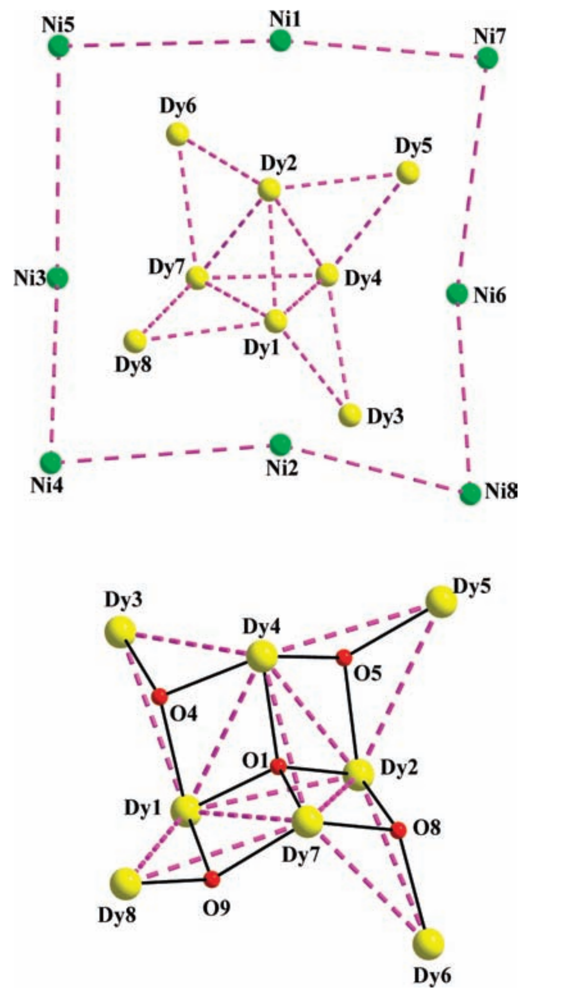


Figure 2. (top) M_{16} topology of the inner Dy_8 cage and the outer Ni_8 shell of complex **1**. (bottom) Inner $[Dy_8(\mu_4\text{-}O^{2-})(\mu_3\text{-}OH^-)_4]$ subcore of **1** highlighting the triangular $[Dy_3(\mu_3\text{-}OH)]$ and tetrahedral $[Dy_4(\mu_4\text{-}O)]$ subunits (purple dashed lines). Color scheme as in Figure 1.

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(15) Crystal structure data for $\mathbf{1}\cdot x$MeOH$\cdot y H_2O$: $C_{351}H_{368}Ni_{16}Dy_{16}N_{114}O_{137}Cl_{10}$, 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, β = 92.81(2)°, 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.

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Dy^{III} of the tetrahedron is linked to two peripheral Dy^{III} by μ-O^- atoms from two η^1:η^1:η^2:μ_3 (type A) pao^- ligands. The Dy···Dy and Dy−O distances are in the ranges 3.547(1)−8.805(4) and 2.075(1)−2.789(9) Å, respectively. If the bridging diatomic oximates are considered part of the inner Dy_8 core, then the latter is $[Dy_8(\mu_4\text{-}O)(\mu_3\text{-}OH)_4(\mu_3\text{-}ONR)_4(\mu\text{-}OR')_8]^{6+}$ (RNO^-, $R'O$ = pao^-; Figure S1 in the Supporting Information).

The outer Ni_8 shell has a nonplanar square-based topology that can be described as comprising a Ni_4 square [Ni4···Ni5, Ni5···Ni7, Ni7···Ni8, and Ni8···Ni4 are 11.623(8), 11.637(3), 11.641(6), and 11.570(2) Å, respectively; Ni···Ni···Ni angles are in the 89.0−89.5° range] and a concentric Ni_4 tetrahedron [Ni···Ni distances and 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_4 square, giving approximately S_4 symmetry for the Ni_8 loop. The chromophores of the Ni^{II} atoms are all $Ni^{II}N_6$. The outer Ni_8 is linked to the inner Dy_8 through 16 μ-NO^- groups from the η^1:η^1:η^1:μ pao^- ligands and through 8 μ_3-NO^- groups from the η^1:η^1:η^2:μ_3 (type A) ligands. Thus, the complete "core−shell" aggregate becomes $[Ni_8Dy_8(\mu_4\text{-}O)(\mu_3\text{-}OH)_4(\mu_3\text{-}ONR)_{12}(\mu\text{-}ONR)_{16}]^{6+}$ (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 π−π interactions.

Complex **1** is the largest metal oxime cluster prepared to date, as well as the first Ni_8Ln_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, $Ni_{54}Gd_{54}$,[17] $Ni_{30}La_{20}$,[18] and $Ni_{21}Ln_{20}$ (Ln = Pr, Nd).[18]

Solid-state direct-current (dc) magnetic susceptibility (χ_M) data on dried **1**·$4H_2O$ were collected in the 5.0−300 K range in an applied field of 0.1 T and are plotted as $\chi_M T$ vs T in Figure 3. The $\chi_M T$ value at 300 K is 128.5 cm^3 K mol^{-1}, essentially equal to the calculated 123.0 cm^3 K mol^{-1} for eight Ni^{II} (S = 1; g = 2.2) and eight Dy^{III} ($^6H_{15/2}$ free ion; $S = {}^5/_2$; L = 5; $g_J = {}^4/_3$) noninteracting ions. It slowly decreases with decreasing temperature down to ~100 K and then rapidly falls to 83.4 cm^3 K mol^{-1} at 5.0 K because of a combination of depopulation of the Stark sublevels of the Dy^{III} $^6H_{15/2}$ state and Ni^{II}···Dy^{III} antiferromagnetic interactions. The $\chi_M T$ value at 5.0 K and the alternating-current (ac) in-phase $\chi_M' T$ value (Figure S4 in the Supporting Information) of ~55 cm^3 K mol^{-1} at 1.8 K indicate significant remaining paramagnetism at the lowest temperatures. The large paramagnetism at 1.8 K and the considerable

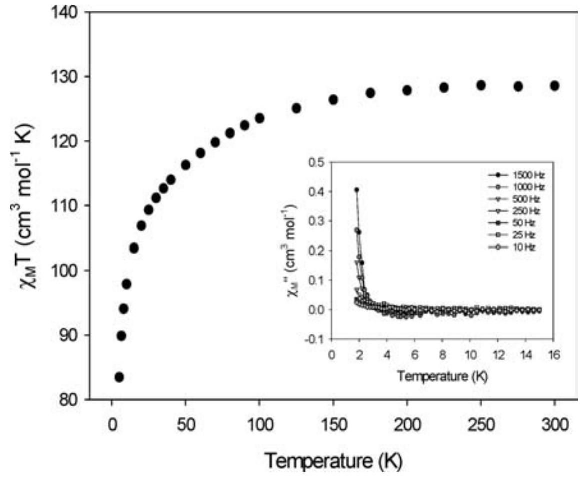

Figure 3. $\chi_M T$ vs T data for **1**·$4H_2O$ in a 0.1 T dc field. (inset) Out-of-phase χ_M'' vs T ac susceptibility signals in a 3.5 G field oscillating at the indicated frequencies.

single-ion anisotropy of Dy^{III} suggested that **1** might be an SMM. At temperatures < 3 K, the ac out-of-phase (χ_M'') susceptibility (Figure 3, inset) displays frequency-dependent signals whose maxima lie below the operating minimum temperature (1.8 K) of our SQUID instrument. This behavior is indicative of slow magnetization relaxation, suggesting **1** to possibly be a new Ni^{II}/Dy^{III} SMM, but one with a rather small relaxation barrier. Further confirmation of the SMM behavior would require single-crystal studies down to 0.04 K, but this was not pursued because there are now many SMMs with such small relaxation barriers.

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_8 and outer Ni_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_8Y_8 and Ni_8Gd_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.

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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.

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