



*Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary*

CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF TWO NEW HETERODINUCLEAR $[\text{Ni}^{\text{II}}\text{Ln}^{\text{III}}]$ COMPLEXES OBTAINED USING A SIDE-OFF COMPARTMENTAL LIGAND AND 2,6-PIRYDIN-DICARBOXYLATO COLIGAND

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Two new heterodinuclear $[\text{Ni}^{\text{II}}\text{Ln}^{\text{III}}]$ complexes, described by the formula $[\text{Ni}^{\text{II}}(\text{valpn})(\text{H}_2\text{O})_2\text{Ln}^{\text{III}}(\text{pdca})(\text{O}_2\text{NO})] \cdot 2\text{H}_2\text{O}$ ($\text{Ln}^{\text{III}} = \text{Ho}$ **1**, Er **2**), have been obtained following the stoichiometric reaction, in a 1:1 molar ratio, between the corresponding $[\text{Ni}^{\text{II}}(\text{valpn})\text{Ln}^{\text{III}}]$ precursors and the dianion of the 2,6-pyridine-dicarboxylic acid [pdca^{2-} = the dianion of 2,6-pyridine-dicarboxylic acid, $\text{H}_2\text{valpn} = 1,3$ -propanediylbis(2-iminomethylene-6-methoxy-phenol)]. The solving of crystal structures revealed discrete dinuclear units, with a 6-coordinate geometry for the Ni^{II} ions and a 9-coordinate geometry for Ln^{III} ions. Magnetic measurements showed a ferromagnetic interaction between the Ni^{II} and Ho^{III} ions.

INTRODUCTION

Molecular magnetism is one of the hot topics in modern chemistry that pushed inorganic synthesis to new heights. The chemistry of 3d-4f heterometallic complexes has risen to an unprecedented level,¹ because the combination of different paramagnetic metal ions within the same molecular entity leads to a wide variety of magnetic properties of the polynuclear complexes.²

The important role played by lanthanide ions in 3d-4f systems is related to their large and, in some cases, highly anisotropic magnetic moments, which can lead to single-molecule magnets (SMMs),³ which can be further assembled into dimers or chains of SMMs.⁴ The ideal candidates

for such systems are Tb^{III} ($^7\text{F}_6$), Dy^{III} ($^6\text{H}_{15/2}$), and Ho^{III} ($^5\text{H}_8$) ions, as even mononuclear Tb^{III} and Dy^{III} complexes which exhibit a slow relaxation of the magnetization have been described.⁵

Among 3d-4f systems, an important class is represented by the 3d-4f heterodinuclear complexes obtained through a synthetic approach developed by Costes.⁶ His strategy relies on the use of dicompartmental Schiff-base ligands derived from *o*-vanillin.⁷ In a two-step process, the 3d metal ion is first coordinated in the N_2O_2 inner site of the organic ligand and then the resulting mononuclear complex is used as ligand to coordinate the 4f ion in the open O_2O_2 site.

The use of the H_2valpn ligand [$\text{H}_2\text{valpn} = 1,3$ -propanediylbis(2-iminomethylene-6-methoxy-phe-

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mol)], allowed us to successfully obtain and characterize various 3d-4f and 3d-3d' dinuclear complexes, exhibiting interesting magnetic^{3g,4,8} and luminescent properties.⁹ Herein, we report the synthesis of two new 3d-4f heterodimetallic systems obtained starting from [Ni^{II}(valpn)Ln^{III}] building blocks and 2,6-pyridine-dicarboxylate anions: [Ni^{II}(valpn)(H₂O)₂Ln^{III}(pdca)(O₂NO)]·2H₂O (Ln^{III} = Ho **1**, Er **2**).

RESULTS AND DISCUSSION

The self-assembly processes between preformed [Ni^{II}(valpn)Ln^{III}] complexes^{3g} and the

dianion of 2,6-pyridine-dicarboxylic acid afforded two new heterodinuclear complexes: [Ni(valpn)(H₂O)₂Ho(pdca)(O₂NO)]·2H₂O **1**, and [Ni(valpn)(H₂O)₂Er(pdca)(O₂NO)]·2H₂O **2**, whose crystal structures are presented in this paper. Magnetic properties of **1** have been investigated.

The two complexes crystallize in the *P2₁/c* monoclinic space group (Table 1). We will describe in detail only the structure of the Ho^{III} derivative, [Ni(valpn)(H₂O)₂Ho(pdca)(O₂NO)]·2H₂O **1**, because the two compounds are isostructural and isomorphous.

Table 1

Crystallographic data, details of data collection, and structure refinement parameters for **1** and **2**

Compound	1	2
Chemical formula	C ₂₆ H ₃₁ O ₁₅ N ₄ NiHo	C ₂₆ H ₃₁ O ₁₅ N ₄ NiEr
<i>M</i> (g mol ⁻¹)	863.19	865.52
Temperature, (K)	293(2)	293(2)
Wavelength, (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	11.0382(6)	11.0510(5)
<i>b</i> (Å)	15.9585(6)	15.9530(8)
<i>c</i> (Å)	18.4166(10)	18.4069(8)
α (°)	90.00	90.00
β (°)	105.735(4)	105.617(3)
γ (°)	90.00	90.00
<i>V</i> (Å ³)	3122.6(3)	3125.3(3)
<i>Z</i>	4	4
<i>D_c</i> (g cm ⁻³)	1.836	1.839
μ (mm ⁻¹)	3.197	3.347
<i>F</i> (000)	1720	1724
Goodness-of-fit on <i>F</i> ²	1.092	1.026
Final <i>RI</i> , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0568, 0.1140	0.0460, 0.0744
<i>RI</i> , <i>wR</i> ₂ (all data)	0.0791, 0.1240	0.0727, 0.0804
Largest diff. peak and hole (eÅ ⁻³)	2.310, -1.470	0.724, -1.518

The crystallographic investigation of **1** revealed neutral [Ni(valpn)(H₂O)₂Ho(pdca)(O₂NO)] dinuclear species (Fig. 1) and crystallization water molecules. The nickel ion occupies the inner coordination site of the Schiff-base ligand. It displays an octahedral environment, with the N₂O₂ equatorial plane built by the donor atoms of the organic ligand [Ni1 – N1 = 2.031(4); Ni1 – N2 = 2.022(4); Ni1 – O2 = 2.025(3); Ni1 – O3 = 2.019(3) Å] and two apical aqua ligands [Ni1 – O1W = 2.102(4); Ni1 – O2W = 2.120(4) Å].

The holmium ion is located the open compartment, being surrounded by eight oxygen and

one nitrogen atoms: two phenolato and two methoxy oxygen atoms from the Schiff-base [Ho1 – O1 = 2.507(4); Ho1 – O2 = 2.297(3); Ho1 – O3 = 2.301(3); Ho1 – O4 = 2.518(4) Å], two oxygen atoms from the chelating nitrate ligand [Ho1 – O9 = 2.429(4); Ho1 – O10 = 2.497(4) Å], the nitrogen atom and two oxygen atoms belonging to the carboxylic groups of the 2,6-pyridine-dicarboxylate [Ho1 – N4 = 2.490(4); Ho1 – O5 = 2.363(4); Ho1 – O7 = 2.401(4) Å]. The intramolecular Ni1...Ho1 separation is 3.459 Å. Selected bond distances for **1** and **2** are given in Table 2.

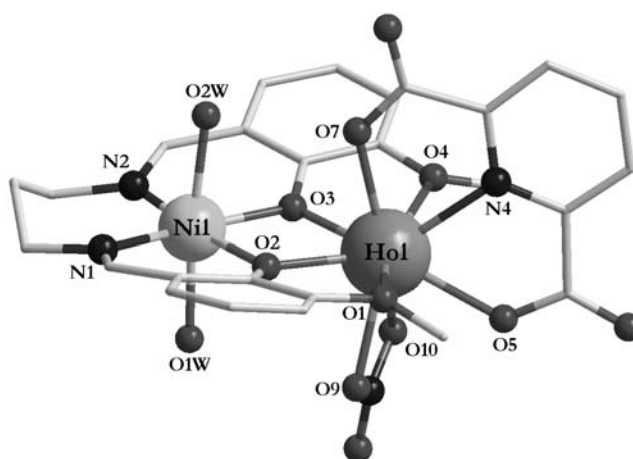


Fig. 1 – View of the molecular structure for [Ni^{II}(H₂O)₂(valpn)Ho^{III}(pdca)(O₂NO)].

Table 2

Selected bond distances (Å) for **1** and **2**

Ni1 – N1	2.031(4)	Ho1 – N4	2.490(4)
Ni1 – N2	2.022(4)	Ho1 – O1	2.507(4)
Ni1 – O2	2.025(3)	Ho1 – O2	2.297(3)
Ni1 – O3	2.019(3)	Ho1 – O3	2.301(3)
Ni1 – O1W	2.102(4)	Ho1 – O4	2.518(3)
Ni1 – O2W	2.120(4)	Ho1 – O5	2.363(4)
		Ho1 – O7	2.401(4)
		Ho1 – O9	2.429(4)
		Ho1 – O10	2.497(4)
Ni1 – N1		Er1 – N4	2.482(4)
Ni1 – N2		Er1 – O1	2.499(3)
Ni1 – O2		Er1 – O2	2.283(3)

Table 2 (continued)

Ni1 – O3	Er1 – O3	2.287(3)
Ni1 – O1W	Er1 – O4	2.511(3)
Ni1 – O2W	Er1 – O5	2.354(3)
	Er1 – O7	2.378(3)
	Er1 – O9	2.419(3)
	Er1 – O10	2.488(4)

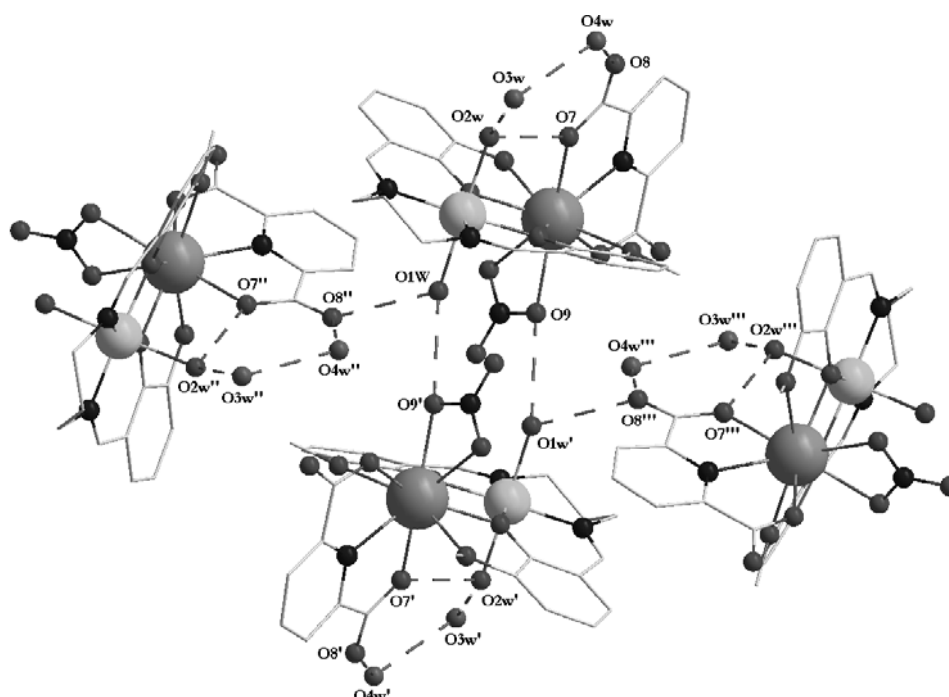


Fig. 2 – View of the structural motif of the 2-D supramolecular architecture formed through hydrogen bonding (' = 1-x, 1-y, 1-z; '' = x, 1.5-y, 0.5+z; ''' = 1-x, -0.5+y, 0.5-z).

A complex 2-D supramolecular architecture is formed through the interplay of various hydrogen bonds established between lattice water molecules [O3w ... O4w = 2.789 Å], lattice water molecules and aqua ligands [O2w ... O3w = 2.730 Å], lattice water molecules and the 2,6-pyridine-dicarboxylate [O4w ... O8 = 2.921 Å], one aqua ligand and the oxygen atom of one chelating nitrate ligand from a neighboring dinuclear unit [O1w ... O9' = 3.003 Å]. The motif of this extended architecture, for the four dinuclear units belonging to a unit cell, is depicted in Fig. 2.

The DC magnetic properties of **1** have been investigated in the 2-300 K range. The temperature variation of the $\chi_M T$ product is represented in Fig. 3.

At room temperature the value of $\chi_M T$ is 14.7 cm³mol⁻¹K, in good agreement to the presence of two uncoupled paramagnetic centers: one Ni^{II} ion ($S = 1$) and one Ho^{III} ion ($S = 2$, $J = 8$, $g_J = 5/4$). When lowering the temperature, $\chi_M T$ decreases continuously down to 15 K, due to the depopulation of the Stark levels of the Ho^{III} ions. Below 13 K, the $\chi_M T$ product slightly increases, reaching a plateau of 12.3 cm³mol⁻¹K in the 10–5 K range. This indicates a ferromagnetic exchange interaction between Ni^{II} and Ho^{III} ions, as previously reported for the dinuclear precursor.^{3g} Below 5 K, the values of the $\chi_M T$ product are decreasing to 9 cm³mol⁻¹K at 2 K, a phenomenon that can be correlated to antiferromagnetic intermolecular interactions.

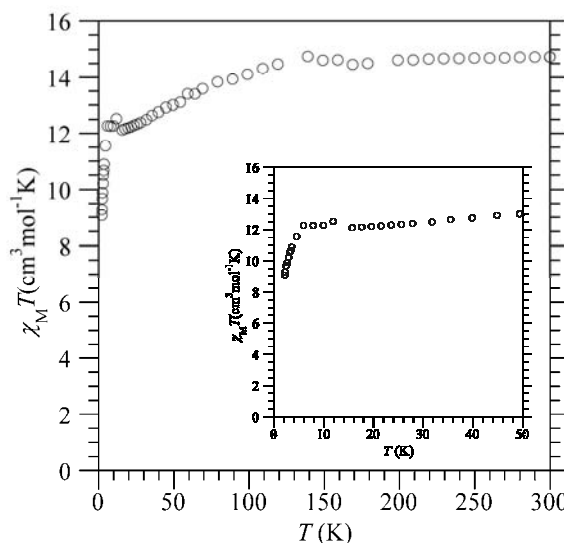


Fig. 3 – Plot of $\chi_M T$ versus T curves recorded for compound **1**. Inset: detail of the low temperature region.

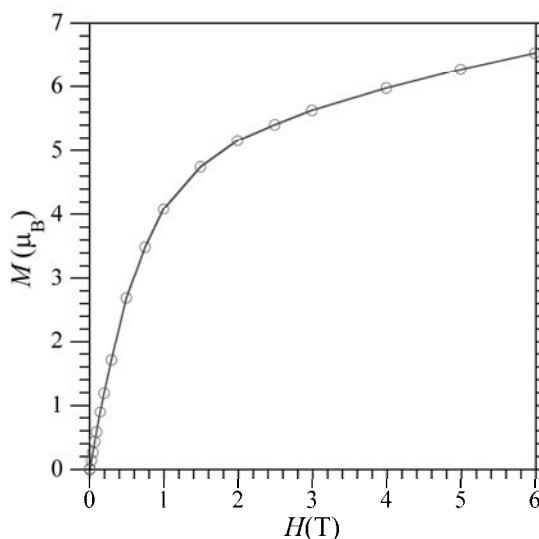


Fig. 4 – Field dependence of the magnetization for **1** measured at $T = 3$ K.

The field dependence of the magnetization has been recorded at $T = 3$ K and the results are reported in Fig. 4. The magnetization increases rapidly up to $5.2 \mu_B$ for an applied field of 2 Tesla. However, saturation is not reached even for the maximum value of the magnetic field ($M = 6.5 \mu_B$ for an $H = 6$ Tesla). The AC magnetic measurements for the holmium derivative (**1**) do not show the Single Molecule Magnet behavior.

EXPERIMENTAL

Materials and methods

All chemicals used, *o*-vanillin, 1,3-diaminopropane, 2,6-pyridine-dicarboxylic acid, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, as well as all solvents were purchased

from commercial sources. All manipulations were performed under aerobic conditions.

The $[\text{Ni}^{\text{II}}(\text{valpn})\text{Ln}^{\text{III}}]$ heterodinuclear complexes were prepared as previously described.^{3g} In order to obtain the $[\text{Ni}^{\text{II}}(\text{valpn})(\text{H}_2\text{O})_2\text{Ln}^{\text{III}}(\text{pdca})(\text{O}_2\text{NO})] \cdot 2\text{H}_2\text{O}$ ($\text{Ln}^{\text{III}} = \text{Ho}$ **1**, Er **2**) complexes, two solutions were mixed in a Berzelius beaker. The first solution was obtained dissolving 0.2 mmol $[\text{Ni}^{\text{II}}(\text{valpn})\text{Ln}^{\text{III}}]$ precursor in 20 mL acetonitrile, while the second one contained 0.2 mmol 2,6-pyridine-dicarboxylic acid and 0.4 mmol $\text{LiOH} \cdot \text{H}_2\text{O}$ dissolved in 10 mL water. The two solutions were mixed and stirred for 30 minutes, before filtering the resulting solution. Green crystals of complexes **1** and **2** were obtained after several days, by slow vaporization of the solvents.

Magnetic measurements

Magnetic data were collected with a Quantum Design MPMS SQUID susceptometer. Samples were obtained from freshly isolated crystals. Magnetic susceptibility measurements were performed in the 2–300 K temperature

range in a 0.1 T applied magnetic field and diamagnetic corrections were applied by using Pascal's constants.

X-ray crystallography and solution of structures

Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the solvent, as described above. Data were collected at 293 K on a STOE IPDS II diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 . The non-H atoms were refined with anisotropic displacement parameters. Drawings of the molecule were performed with the program Diamond 3. A summary of the crystallographic data and the structure refinement is given in Table 1. CCDC reference numbers: 850701 (1) and 850702 (2).

CONCLUSIONS

The two new complexes, herein described, illustrate the versatility of $[\text{Ni}^{\text{II}}(\text{valpn})\text{Ln}^{\text{III}}]$ complexes in generating new and interesting compounds. The investigation of the magnetic properties of the holmium derivative reveals a ferromagnetic interaction between Ni^{II} and Ho^{III} ions, in line with the one we have previously reported for the $[\text{Ni}^{\text{II}}(\text{valpn})\text{Ho}^{\text{III}}]$ starting material.^{3g}

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