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# High Nuclearity in Azido/Oximate Chemistry: $Ni_{14}$ and $Ni_{13}$ Clusters with $S$ = 6 and 9 Ground States

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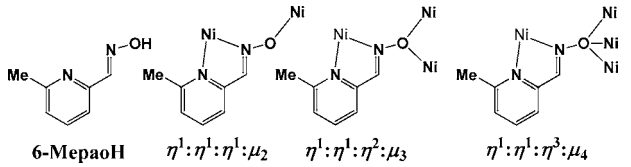
Supporting Information

**ABSTRACT:** In the present work, we report a family of $Ni_{14}$ and unprecedented $Ni_{13}$ clusters linked by end-on azido and oximato bridges. Ferrimagnetic response gives $S$ = 6 and 9 ground states, resulting in the largest nuclearities and spins in nickel oximato chemistry.

Coordination chemistry of salicyl[1] or pyridyl[2] oximate ligands has grown in the past decade in relation to their ability to generate high-nuclearity metallic clusters with single-molecule-magnet (SMM) response. Blending of different bridging ligands (other than carboxylates) is a synthetic strategy widely employed in cluster chemistry to increase the nuclearity or to improve the magnetic properties of the resulting complexes. The azido anion (in its end-on coordination mode) has been intensely studied to obtain ferro- or ferrimagnetic high-spin systems with a large variety of coligands.[3]

Following our previous work in nickel/oximato/azide chemistry, we have centered our attention on the poorly explored ligand 6-methylpyridine-2-carbaldehydeoxime (6-MepaoH; Chart 1), for which, in addition to one early reported[4] $Ni^{II}_9$ cluster, only some $Ni_5$ and $Ni_6$ cages[5] and one $(Mn^{II}_2Mn^{III}_2)_n$ chain[6] have been recently characterized by us. The reaction of 6-MepaoH with $Ni^{II}$ salts in the presence of sodium azide yields clusters with the formulas $[Ni_{13}(6\text{-Mepao})_{12}(N_3)_8(OH)_6(N\text{-Meen})_2(MeOH)_4]$ (**1**·7MeOH·2-$H_2O$; N-Meen = *N*-methylethylenediamine), $[Ni_{13}(6\text{-Mepao})_{12}(N_3)_8(OH)_6(MeOH)_8]$ (**2**), and $[Ni_{14}(6\text{-Mepao})_{12}(N_3)_8(Cl)_2(OH)_4(MeOH)_4(H_2O)_4]Cl_2$ (**3**·7MeOH·2.5$H_2O$).

**Chart 1. 6-MepaoH Ligand and Coordination Modes Found in 1−3**




Compounds **1**−**3**, together with the previously reported complexes $[Ni_{12}Na_2(OH)_4(N_3)_8(pao)_{12}(H_2O)_{10}](OH)_2$ (**4**) and $[Ni_{14}(OH)_4(N_3)_8(pao)_{14}(paoH)_2(H_2O)_2](ClO_4)_2$ (**5**),[7] form a family of ferrimagnetic clusters with common structural features. The maximum ground state $S$ = 9 has been found for the $Ni_{13}$ compounds **1** and **2**.

The largest nuclearities reported until now in nickel oximato chemistry were $Ni_{12}$ and $Ni_{14}$, which also exhibit the previous record spin $S$ = 6.[7,8] It is worth noting that the nuclearity for $Ni_{13}$ is extremely rare, and to our knowledge, only one nickel triazole cluster exhibiting this nuclearity has been reported until now.[9]

A first approach to the family of clusters **1**−**5** can be made by attending to their common structural motifs. All of them contain two hexanuclear $Ni_6$ rings, which acting as complex as the ligand link two $Na^+$ cations ($Ni_6Na_2Ni_6$, **4**), one $Ni^{2+}$ cation ($Ni_6NiNi_6$, **1** and **2**), or two $Ni^{2+}$ cations ($Ni_6Ni_2Ni_6$, **3** and **5**); see Figure 1. In addition to **1**−**5**, one hexanuclear $[Mn^{III}Ni_5(N_3)_4(pao)_6(paoH)_2(OH)_2](ClO_4)$ system with the same local topology and $pao^-$ ligands has recently been reported.[10]

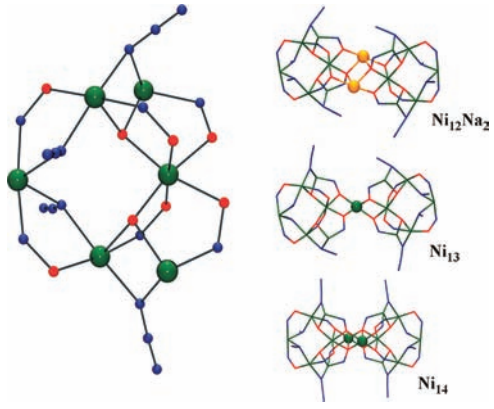



**Figure 1.** (Left) Plot of the common $Ni_6$ ring for **1**−**5**. (Right) Schematic core of $Ni_{12}Na_2$, $Ni_{13}$, and $Ni_{14}$ clusters exhibiting a very similar pattern. Color key: Ni, green; O, red; N, blue; Na, orange.

Complexes **1** and **2** are isostructural,[11] and thus only **1** will be described in detail. Complex **1** consists of two $\{Ni_5(6\text{-Mepao})_6(N_3)_4\}$ fragments connected by one nickel linear trinuclear unit (Figure 2). The nickel atoms of these $Ni_5$ fragments are linked by end-on azido/oximato bridges between

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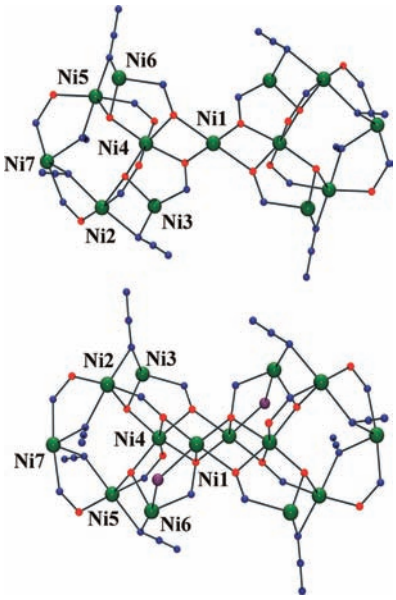


**Figure 2.** (Top) Core of clusters **1** and **2**. (Bottom) Core of cluster **3**. Color key: Ni, green; O, red; N, blue; Cl, violet.

Ni(2)/Ni(7) and Ni(5)/Ni(7) or end-on azido/hydroxo bridges between Ni(2)/Ni(3) and Ni(5)/Ni(6). Two $\eta^1{:}\eta^1{:}\eta^1{:}\mu_2$-oximates and two $\mu_3$-OH bridges link Ni(2,5) with Ni(4), and the core is completed with two $\eta^1{:}\eta^1{:}\eta^2{:}\mu_3$-oximate bridges [linking Ni(3,6) with Ni(4) and the central Ni(1) atom] and solvent molecules. The N-Meen ligand is linked to Ni(6). The Ni−N−Ni bond angles involving azido ligands show values of 94.6(3)° and 99.0(3)° for Ni(2)−N−Ni(3) and Ni(5)−N−Ni(6) and larger ones [111.0(3)° and 117.3(3)°] for Ni(7)−N−Ni(2) and Ni(7)−N−Ni(5). Ni−N−O−Ni torsion angles are lower than 7° except for Ni(3)−N−O−Ni(4), which has a value of 28.5(7)°. The only difference among **1** and **2** lies in the substitution of the bidentate amine on Ni(6) by two methanol molecules.

Tetradecacomplex[11] **3** is very similar to the previously reported **5**, and the reader can find a detailed description of its core in a corresponding publication.[7] The main differences are substitution of the neutral bidentate paoH ligands on Ni(2) and the bridging pao$^-$ bridges in **5** by two methanol molecules and two chloride bridges in **3**. The remaining bond parameters are very similar in both compounds.

The differences between the $Ni_{13}$ (**1** and **2**) and $Ni_{14}$ (**3** and **5**) cores are induced by the subtle change in the coordination mode of the 6-Mepao$^-$ ligands linked to Ni(2) and Ni(6). In the $Ni_{13}$ cluster, the oxime coordinated to Ni(2) ($\eta^1{:}\eta^1{:}\eta^1{:}\mu_2$ mode) does not interact with the central nickel atom and the oxime coordinated to Ni(6) ($\eta^1{:}\eta^1{:}\eta^2{:}\mu_3$ mode) links Ni(6) with Ni(4) and the central Ni(1) cation. In contrast, in the $Ni_{14}$ cluster, the oximes coordinated to the Ni(2) and Ni(6) clusters adopts the $\eta^1{:}\eta^1{:}\eta^2{:}\mu_3$ and $\eta^1{:}\eta^1{:}\eta^3{:}\mu_4$ modes, linking Ni(4) and two central atoms Ni(1) and Ni(1′) (Figure 3). The increase of the coordination sites in the central fragment of the cluster is fulfilled with the chloro bridges and solvent molecules.

The room temperature $\chi_M T$ value for **1** is 13.7 cm$^3$ K mol$^{-1}$, close to the expected value for 13 isolated $Ni^{2+}$ ions (13.0 cm$^3$ K mol$^{-1}$). Upon cooling, $\chi_M T$ decreases very slightly, exhibiting a broad minimum at 160 K and suggesting ferrimagnetic response. Below the minimum, the plot reaches a maximum $\chi_M T$ value of 20.1 cm$^3$ K mol$^{-1}$ at 9 K, followed by a fast decrease to 12.6 cm$^3$ K mol$^{-1}$ (Figure 4). Compound **2** shows a quasi-identical behavior (Figure S2 in the Supporting Information).

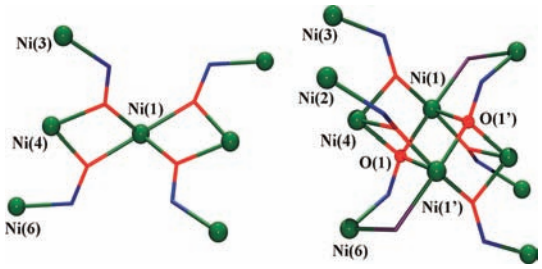


**Figure 3.** Coordination to the central nickel atoms of the oximate bridging ligands for the $Ni_{13}$ (left) and $Ni_{14}$ (right) clusters.

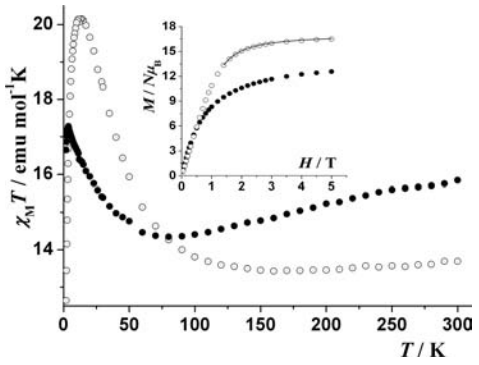


**Figure 4.** $\chi_M T$ product versus $T$ plot for compounds **1** (open circles) and **3** (solid circles). Inset: magnetization experiments at 2 K showing the high-field fit of the data (solid line).

Compound **3** shows a room temperature $\chi_M T$ value of 15.8 cm$^3$ K mol$^{-1}$ (slightly larger than that expected for 14 $Ni^{2+}$ isolated ions, 14.0 cm$^3$ K mol$^{-1}$). $\chi_M T$ decreases upon cooling, exhibiting a clear minimum of 14.3 cm$^3$ K mol$^{-1}$ at 80 K. Below the minimum, the plot increases up to a maximum $\chi_M T$ value of 17.3 cm$^3$ K mol$^{-1}$ at 3.7 K and finally slightly diminishes to 16.4 cm$^3$ K mol$^{-1}$ at 2 K. The size of **1**−**3** and the large number of superexchange pathways exclude fit of the data, but an approach to the main interactions can be made on the basis of the structural parameters.

As described, these compounds can be envisaged as two pentanuclear $Ni^{II}$ wings linked by a linear $Ni_3$ or butterfly-like $Ni_4$ subunits. Nickel atoms from both wings are connected by double oximato/end-on azido or $\mu_3$-OH/end-on azido bridges. There is experimental evidence that the double oximato/end-on azido bridges promote ferromagnetic coupling,[12] and experimental and theoretical density functional theory calculations also indicate that ferromagnetic coupling should be expected for the double $\mu_3$-OH/end-on azido bridges.[13] Thus, we have that each wing should be ferromagnetically coupled with an $S = 5$ local spin. The interaction of Ni(2,3,5,6) with Ni(4), mediated by double $\mu_{2,3}$-oximato and $\mu_3$-OH bridges (with Ni−O−Ni angles of around 111° in all cases), should provide an antiferromagnetic contact, and finally the interaction between Ni(4) and Ni(4′) with the central Ni(1) atom should be antiferromagnetic in nature according the double Ni−O−Ni linkage with bond angles of 103.2(2)° and 109.9(2)°. Given all of these coupling interactions, we assume that **1** must have a


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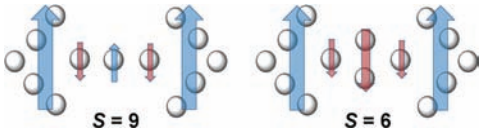
ground state of $S = 9$ according the spin alignment shown in Chart 2, left.

**Chart 2. Scheme of the Spin Alignment of 1 and 2 (Left) and 3 (Right) and the Proposed Spin Ground States**




The lower $\chi_M T$ value observed for **3** is compatible with an $S = 6$ ground state arising from the antiferromagnetic coupling between the ferromagnetic $Ni_5$ wings and the ferromagnetic central $Ni_4$ butterfly. This proposal agrees with the $S = 6$ ground state proposed by Christou et al.[7] for complex **5** and the $S = 3$ ground state reported for the $\{Mn^{III}Ni_5\}$ related system.[10] From experimental evidence, substitution of the oximate bridge in **5** by one bridging chloride in **3** does not modify the magnetic response of the cluster.

This proposal was confirmed by magnetization experiments at 2 K. Magnetization of **1** and **2** shows a fast increase with quasi-saturated values equivalent to 16.5 and 17.2 electrons (Figures 4 and S2 in the Supporting Information). The low-field magnetization of **1** is slightly sigmoidal, showing a maximum at 0.3 T in its first derivative and suggesting an intercluster interaction close to $-0.3$ cm$^{-1}$. A fit of the magnetization data above 1.5 T (to discard the intercluster interaction effect) gives an excellent fit for an $S = 9$ spin with a low $D$ value of $-0.15$ cm$^{-1}$ (Figure 4, inset). Thus, the low-$T$ decay in the $\chi_M T$ plot can be attributed to intercluster interactions mainly mediated by hydrogen bonds. Magnetization for **3** tends to be equivalent to 12.6 electrons, in good agreement with the proposed $S = 6$ ground state and the reported data for **5**.

Despite the large $S = 9$ ground state, the low $D$ value, arising partially from the $C_2$ symmetry of the molecule, excludes the observation of out-of-phase signals and a SMM response of over 2 K, as was experimentally checked by alternating-current susceptibility measurements.

In conclusion, the new topology of the $\{Ni_{13}\}$ clusters completes a family of clusters exhibiting the largest nuclearity and spin ground states in nickel/oximate chemistry. These complexes provide new examples of the relevant versatility of the oxime ligands to generate high-nuclearity systems and the ability of the azido ligand to promote selective ferromagnetic interactions.

## ■ ASSOCIATED CONTENT

### Supporting Information

X-ray crystallographic data for complexes **1** and **3** in CIF format, experimental procedures, and structural and magnetic data for compound **2** (Figures S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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(11) Crystal data for $1 \cdot 7MeOH \cdot 2H_2O$: $C_{94}N_{52}Ni_{13}O_{22}H_{116} \cdot (CH_4O)_7(H_2O)_2$ (3353.98), monoclinic, $C2/c$, $a = 24.582(13)$ Å, $b = 22.488(8)$ Å, $c = 27.802(10)$ Å, $\beta = 91.96(2)°$, $V = 15360(11)$ Å$^3$, $Z = 4$, $T = 100(2)$ K, $\lambda$(Mo K$\alpha$) = 0.71073 Å, 23067 reflections collected, 14280 unique ($R_{int} = 0.0446$), $R = 0.0611$, $R_w^2 = 0.1587$. Crystal data for $3 \cdot 7MeOH \cdot 2.5H_2O$: $C_{88}H_{96}Cl_4N_{48}Ni_{14}O_{24} \cdot (CH_4O)_7(H_2O)_{2.5}$ (3497.25), triclinic, $P\bar{1}$, $a = 16.227(1)$ Å, $b = 16.709(2)$ Å, $c = 19.201(2)$ Å, $\alpha = 108.409(5)°$, $\beta = 92.219(5)°$, $\gamma = 115.014(4)°$, $V = 4385.7(7)$ Å$^3$, $Z = 1$, $T = 100(2)$ K, $\lambda$(Mo K$\alpha$) = 0.71073 Å, 17249 reflections collected, 17249 unique ($R_{int} = 0.0426$), $R = 0.0424$, $R_w^2 = 0.1380$. Cell data for **2**: monoclinic, $C2/c$, $a = 24.525(5)$ Å, $b = 22.274(5)$ Å, $c = 27.632(6)$ Å, $\beta = 92.96(1)°$, $V = 15074(1)$ Å$^3$. CCDC deposition numbers for **1** and **3**: 867793 and 867794.

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