

The highest nuclearity metal oxime clusters: Ni₁₄ and Ni₁₂Na₂ complexes from the use of 2-pyridinealdoximate and azide ligands†‡

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The reactions of 2-pyridinealdoxime [(py)CHNOH] with Ni(ClO₄)₂·6H₂O in the presence of NaOH and NaN₃ have led to Ni^{II}₁₄ and Ni^{II}₁₂Na₂ clusters; the Ni₁₄ compound is the biggest metal oxime cluster discovered to date, as well as the largest Ni azide cluster.

There continues to be great interest by groups around the world in the synthesis and characterization of high-nuclearity 3d molecular clusters. Among the diverse reasons for this are the search for models of metal-containing biological sites,¹ and new high-spin clusters and single-molecule magnets.^{2,3} There thus continues to be a need for new synthetic methods to such molecules. One fertile approach is to use chelates containing alkoxide⁴ or oximate^{5,6} groups, since these are good bridging groups that can foster formation of polynuclear products. Oximates have been employed in the synthesis of smaller nuclearity homo- or heterometallic clusters and chains with interesting magnetic properties.^{5,7} 2-Pyridyl oximes,⁸ (py)C(R)NOH (R = H, Me, Ph, py, *etc.*), are a subclass of oximes that have yielded some 3d metal complexes,^{5b,9–12} only very few of which are in Ni chemistry.¹³ In the present work, we report some interesting Ni clusters from the use of 2-pyridinealdoxime (paoH; pyridine-2-carbaldehyde oxime; (py)CHNOH). This ligand previously gave the triangular complex [Ni₃(pao)₅(paoH)]⁺¹⁴ and the enneanuclear complex [Ni₉(OH)₄(pao)₁₀(H₂O)₈]⁴⁺ (**1**).¹⁵ We have now discovered synthetic routes into significantly higher nuclearity species, which in addition possess interesting magnetic properties. We believe this work presages a rich new area of higher nuclearity metal oxime products than is currently known.

The present results were initially part of an investigation into the possible replacement of some or all of the OH[−] bridges in **1** with end-on N₃[−] bridges in order to increase its *S* = 1 ground state by introducing ferromagnetic interactions.^{15,16} However, reactions of pre-isolated salts of **1** with N₃[−] under a variety of conditions gave mixtures of products. We thus decided instead to broaden the work into a systematic investigation of Ni^{II}/paoH reactions in the presence of azide, and this led to the present results. The reaction between Ni(ClO₄)₂·6H₂O and 1 equivalent of paoH in H₂O gave an olive-green solution. The pH was adjusted to 8.0 using aqueous

NaOH (1 M), and the solution was then treated with 2 equivalents of NaN₃ in H₂O to give an olive-green precipitate. Recrystallization from an MeCN solution layered with Et₂O–Me₂CO (1 : 1) gave crystals of [Ni₁₄(OH)₄(N₃)₈(pao)₁₄(paoH)₂(H₂O)₂](ClO₄)₂ (**2**) as 2·8Me₂CO·4Et₂O·12H₂O in 15% yield (based on the ligand).[§] Slow evaporation of the filtrate at room temperature gave after 3 d orange crystals of [Ni₁₂Na₂(OH)₄(N₃)₈(pao)₁₂(H₂O)₁₀](OH)₂ (**3**) as 3·6Et₂O in yields up to 60%.[§] Using NBu₄⁺N₃[−] and NEt₃ in place of NaN₃ and NaOH, respectively, precludes formation of **3** and gave only **2** in a much higher yield of 65%.

The centrosymmetric cation[¶] of **2** (Fig. 1) consists of fourteen distorted octahedral Ni^{II} atoms held together by four μ₃-OH[−] ions (O1, O2, O1', O2'), eight end-on doubly bridging (η¹-μ) N₃[−] ions, and eight η¹:η¹:η¹-μ, four η¹:η¹:η²-μ₃ and two η¹:η¹:η³-μ₄ pao[−] groups (Chart 1); the latter is a novel binding mode for pao[−].⁸ In addition, there are two chelating (η²) paoH groups on Ni7 and Ni7', and terminal H₂O ligands on central Ni4 and Ni4'. The core (Fig. 2, top) can be conveniently described as consisting of a central [Ni₄(μ₃-OR)₂(μ-OR)₄]²⁺ defective double-cubane subunit (RO[−] = pao[−]) linked to two [Ni₅(μ-N₃)₄(μ-OH)₂]⁴⁺ subunits *via* the two OH[−] groups of the latter, which become μ₃ (Fig. S1 in ESI[†]). The Ni–N_{azido}–Ni angles are in the 94.8(6)–111.1(5)[°] range.

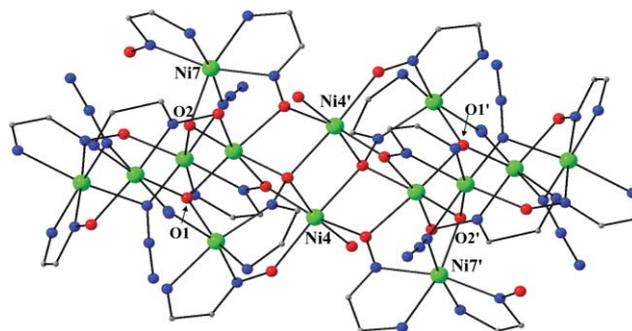


Fig. 1 Molecular structure of the cation of **2**. To avoid congestion, most carbon atoms of the sixteen paoH and pao[−] ligands have been omitted. Colour code: Ni green, O red, N blue, C grey.

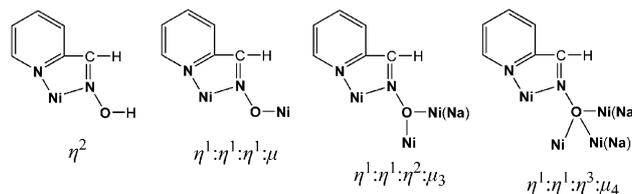


Chart 1 The crystallographically established coordination modes of paoH and pao[−] in complexes **2** and **3**.

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‡ Electronic supplementary information (ESI) available: Subunits of **2** and **3**, and the molecular structure of the cation of **3**. See DOI: 10.1039/b708189h

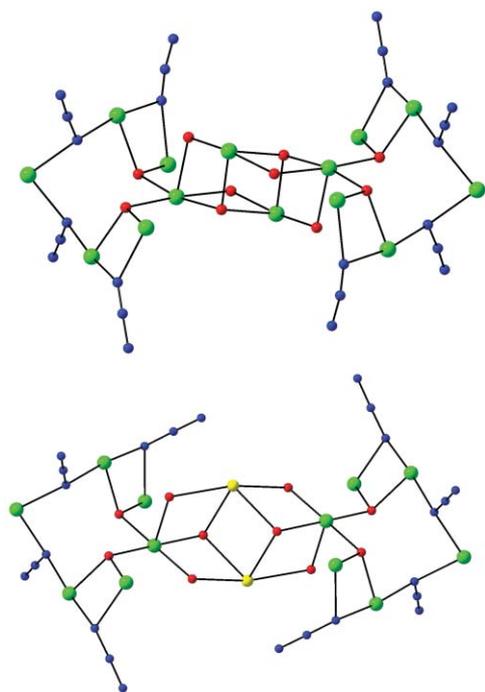


Fig. 2 The core of complexes **2** (top) and **3** (bottom). Color code: Ni green, Na yellow, O red, N blue.

Complex **2** is the largest metal/oxime cluster discovered to date, as well as the first Ni₁₄ complex and the largest Ni^{II}/N₃⁻ cluster.

The structure of **3** consists of a centrosymmetric [Ni₁₂Na₂(OH)₄(N₃)₈(pao)₁₂(H₂O)₁₀]²⁺ cation (Fig. S2 in ESI) and hydrogen-bonded OH⁻ counterions. The core is [Ni₁₂Na₂(μ-N₃)₈(μ₃-OH)₄(μ₃-OR)₂(μ-OR)₄]⁸⁺ (Fig. 2, bottom). The cation is thus structurally very similar to that of **2**, the only differences being: (i) the replacement of two η¹:η¹:η¹-μ pao⁻ and the two η² paoH ligands of **2** by eight terminal H₂O ligands in **3**, and the replacement of the two central octahedral Ni4 and Ni4' atoms of **2** with two square pyramidal Na⁺ ions in **3** (Na...Na = 3.457(1) Å); and (ii) a twist of the central {Na₂O₂} rhomb in **3** versus the {Ni₂O₂} rhomb in **2** (Fig 2). Complex **3** joins only a very small family of structurally characterized Ni^{II}/Na^I clusters.¹⁷

The solid-state dc magnetic susceptibilities (χ_M) of **2** and **3** were measured in the 5.0–300 K range in a 1 kG (0.1 T) field, and they are plotted as χ_MT vs T in Fig. 3. χ_MT at 300 K is 21.07

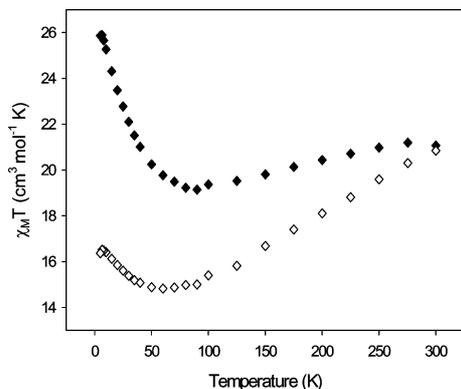


Fig. 3 Plot of χ_MT vs T for complexes **2** (◆) and **3** (◇).

and 20.84 cm³ mol⁻¹ K for **2** and **3**, respectively, higher than the 16.94 cm³ mol⁻¹ K value (for g = 2.2) expected for a cluster of 14 non-interacting Ni^{II} ions, indicating the presence of dominant ferromagnetic exchange interactions. As T is lowered, χ_MT for both complexes gradually decreases to a minimum at 90 and 60 K, respectively, and then increases to 25.89 cm³ mol⁻¹ K at 6.5 K for **2** and 16.52 cm³ mol⁻¹ K at 6.5 K for **3**. The shape of the curves and their χ_MT values are consistent with both ferro- and antiferromagnetic interactions, promoted by the eight end-on N₃⁻ groups¹⁸ and the bridging OH⁻/oximate groups,^{6,14,15} respectively. Assuming typical g values for Ni^{II} of 2.2–2.3, the 6.5 K values for **2** and **3** are as expected for an S = 6 species and two essentially non-interacting S = 3 Ni₆ species, respectively.

To confirm these ground state spin estimates, magnetization (M) data were collected in the 0.1–4 T and 1.8–10.0 K ranges, and these are plotted as M/Nμ_B vs H/T for **2** in Fig. 4. The data were fit by matrix diagonalization to a model that assumes only the ground state is populated, includes axial zero-field splitting (DS_z²) and the Zeeman interaction, and carries out a full powder average. The best fit (solid lines in Fig. 4) gave S = 6, g = 2.17 and D = -0.12 cm⁻¹. The fits for S = 5 and 7 were unacceptable, giving g > 2.50 and g < 1.90, respectively. Fields > 4 T were ignored to avoid complications from low-lying excited states. For **3**, good fits of the magnetization data could not be obtained, presumably due to greater complications from low-lying excited states as expected for two weakly interacting halves of the molecule. Similar problems have been reported for other Ni^{II}_xNa_y clusters.¹⁹

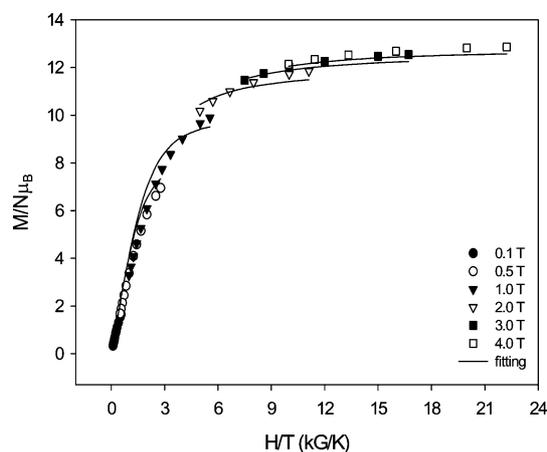


Fig. 4 Plot of reduced magnetization (M/Nμ_B) vs H/T for complex **2** in the temperature range 1.8–10 K and at the indicated fields. Solid lines are the fit; see the text for the fit parameters.

For a further assessment of the ground state spins of the complexes, complications from the applied dc field were removed completely by carrying out ac susceptibility measurements with a 3.5 Oe ac field oscillating at frequencies up to 1000 Hz. The in-phase ac signals (χ_M') are plotted as χ_M'T in Fig. 5; no out-of-phase signals (χ_M'') were observed above 1.8 K, the operating minimum of the SQUID magnetometer. Extrapolation of χ_M'T to 0 K, where only the ground state is populated, and by using data above ~6 K (to avoid the lower temperature drops due to intermolecular interactions, zero-field splitting, etc.) gave ~23.5 and ~7.8 cm³ mol⁻¹ K for **2** and for each Ni₆ subunit of **3**, respectively. These confirm an S = 6 ground state with g ~ 2.12 for

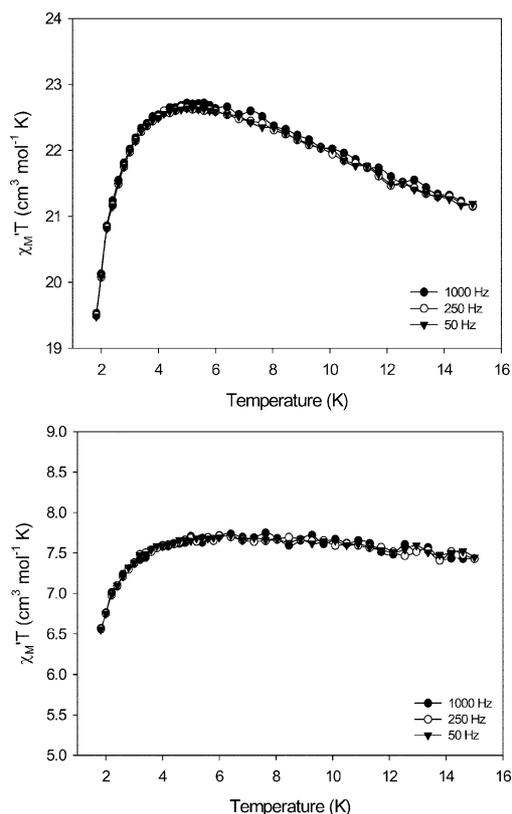


Fig. 5 In-phase ac susceptibility (χ_M' , as χ_M'/T) vs T at the indicated frequencies for complexes **2** (top) and **3** (bottom, per Ni_6 subunit).

2, and an $S = 3$ ground state with $g \sim 2.28$ for each half of **3**. Owing to the size and complexity of the Ni_x cores, it is not possible to unequivocally rationalize these ground states, especially since there are likely competing exchange interactions and spin frustration effects operative.

In summary, the use of both azide and paoH in reactions with Ni^{II} sources has led to the highest nuclearity metal/oxime cluster to date, showing that tridentate oximes can indeed support high nuclearity chemistry when coupled with appropriate ancillary groups. The obtained products are novel in multiple ways, as described, but they also provide a rare example of a complicated structural type where central paramagnetic ions have been replaced with diamagnetic ones with little impact on the structure. This should lead to deeper insights into the nature of the intramolecular exchange interactions and spin frustration as the complexes are analyzed in greater detail; for example, how the two $S = 3$ Ni_6 subunits of **3** couple with two additional $S = 1$ Ni atoms to give the $S = 6$ Ni_{14} complex **2**. Further studies are in progress.

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Notes and references

§ Vacuum-dried samples of both compounds analysed as **2** and $3 \cdot 2\text{H}_2\text{O}$. Calcd (found) for **2**: C, 33.91 (33.76); H, 2.67 (2.75); N, 23.07

(22.97%). Calcd (found) for $3 \cdot 2\text{H}_2\text{O}$: C, 30.26 (30.22); H, 3.17 (3.26); N, 23.52 (23.37%).

¶ Crystal data for $2 \cdot 8\text{Me}_2\text{CO} \cdot 4\text{Et}_2\text{O} \cdot 12\text{H}_2\text{O}$: $\text{C}_{116}\text{H}_{148}\text{Ni}_{14}\text{Cl}_2\text{N}_{56}\text{O}_{42}$, $M_w = 3891.74$, triclinic, space group $P\bar{1}$ with $a = 17.143(6)$, $b = 20.214(7)$, $c = 25.715(9)$ Å, $\alpha = 83.379(7)$, $\beta = 82.208(7)$, $\gamma = 65.901(8)^\circ$, $V = 8041(5)$ Å³, $T = 173(2)$ K, $Z = 2$, $R1 [I > 2\sigma(I)] = 0.0828$, $wR2 = 0.1813$ (F^2 , all data). Crystal data for $3 \cdot 6\text{Et}_2\text{O}$: $\text{C}_{96}\text{H}_{144}\text{Ni}_{12}\text{Na}_2\text{N}_{48}\text{O}_{34}$, $M_w = 3265.09$, triclinic, space group $P\bar{1}$ with $a = 13.7676(12)$, $b = 16.2729(14)$, $c = 17.5222(14)$ Å, $\alpha = 102.327(2)$, $\beta = 108.530(2)$, $\gamma = 107.775(2)^\circ$, $V = 3328.3(5)$ Å³, $T = 173(2)$ K, $Z = 1$, $R1 [I > 2\sigma(I)] = 0.0352$, $wR2 = 0.0615$ (F^2 , all data). CCDC reference numbers 640087 and 640088. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708189h

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