Cluster Chemistry

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Structural Effects of Sodium Cations in Polynuclear, Multicubane-Type Mixed Na–Ni Complexes**

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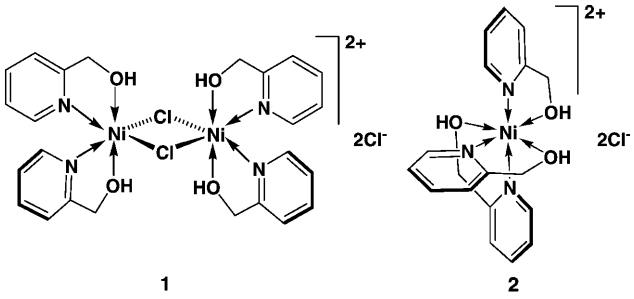
Dedicated to Professor Herbert W. Roesky on the occasion of his 75th birthday

The importance of transition-metal catalysts for ethylene oligo- and polymerization continues to motivate the synthesis of a wide range of heterotopic ligands and metal complexes.[1] Studies of dinuclear Ni^{II} complexes with N,OH chelates as precatalysts for ethylene oligomerization[2] triggered our interest in comparing complexes with (pyridine-2-yl)methanol (HL) and those containing the corresponding anionic chelate, partly because N,O^- ligands may lead to systems that do not require any cocatalyst.[3] Furthermore, L^- is well known to promote the formation of polynuclear complexes with exciting physical properties,[4] paralleling the rich chemistry of 2-pyridones.[5] We have now obtained unusual mixed nickel/sodium polynuclear complexes and identified remarkable structural effects of the sodium cations associated with the reagent used to deprotonate the alcohol function. In addition to their intrinsic novelty, such observations are relevant to the possible in situ formation of unexpected and possibly overlooked active species in catalytic reactions.

The dinuclear complex $[Ni(\mu\text{-}Cl)(HL)]_2Cl_2$ (**1**) and the mononuclear, octahedral *mer*-$[Ni(HL)_3]Cl_2$ complex (**2**) have been recently reported.[2a] The reaction of **1** with 10 equivalents of NaH in THF led mainly to a complex catalytically active for ethylene oligomerization formulated as



1 **2**

$[Ni(HL)(L)Cl]$,[2a] but a few green crystals were also obtained, which are now shown to correspond to a very unusual mixed Ni–Na cluster (Figures 1 and 2).

In this cluster, **3**,[20] two fragments are held together through $Na^+\cdots O$ interactions (Figure 2 left): 1) a cationic trinuclear nickel moiety (Ni2, Ni3, Ni4, Figure 1b), in which two L^- ligands N,O-chelate each metal center, the Ni atoms being doubly bridged by the oxygen atoms and further capped by a μ_3-OH group; and 2) a mononuclear anionic unit in which three N,O chelating ligands form a facial arrangement around Ni1 (Figure 1c). The alcoholate oxygen atoms O5, O7, and O9 each bridge two Na^+ ions and two Ni centers in the Ni_3 substructure. This generates a pseudo-cubane arrangement for Ni2, Ni3, Ni4, the μ_3-OH group (O10-H), and a missing vertex (Figure 2). The latter is shared with another defective pseudo-cubane entity containing Ni1, the three Na^+ ions, and O1, O2, and O3, which each bridge two Na^+ ions. The formation of this unprecedented nickel/sodium polynuclear complex illustrates the remarkable effect of the Na^+ ions.[5f,6]

A much improved synthesis of **3** was devised by reacting HL, $[NiCl_2(DME)]$ (DME = 1,2-dimethoxyethane), and NaH in THF in a 3.2:1:5 ratio, respectively. The presence of the μ_3-OH group most likely originates from the presence of NaOH that originates from NaH [Eq. (1), see the Supporting Information for details].

$$4\,[NiCl_2(DME)] + 9\,HL + 9\,NaH + NaOH \rightarrow [Ni_4Na_3(L)_9OH]Cl\,(\mathbf{3}) + 7\,NaCl\downarrow + 9\,H_2\uparrow + 4\,DME \quad (1)$$

When HL was stirred in THF with $[NiCl_2(DME)]$ for 12 h, **1** formed first, irrespective of the L/Ni ratio. Complex **2** was not observed under these conditions, even when a 3:1 L/Ni ratio was used. Unexpectedly, isolated **1** does not readily react

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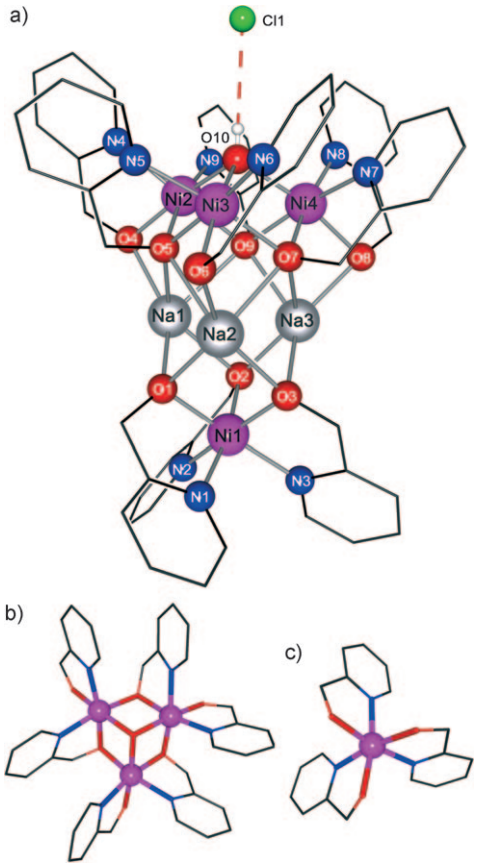

Figure 1. a) Structural diagrams of $[\{Ni(PyCH_2O)\}_3(\mu_2\text{-}OCH_2Py)_3(\mu_3\text{-}OH)(\mu_5\text{-}Na)_3\{Ni(PyCH_2O)_3\}]Cl$ (**3**), b) and c) $[Ni_3L_6(\mu_3\text{-}OH)]$ and NiL_3 moieties, respectively (hydrogen atoms omitted). Color code: C: black, Cl: green, N: blue, Na: gray, Ni: violet, O: red.

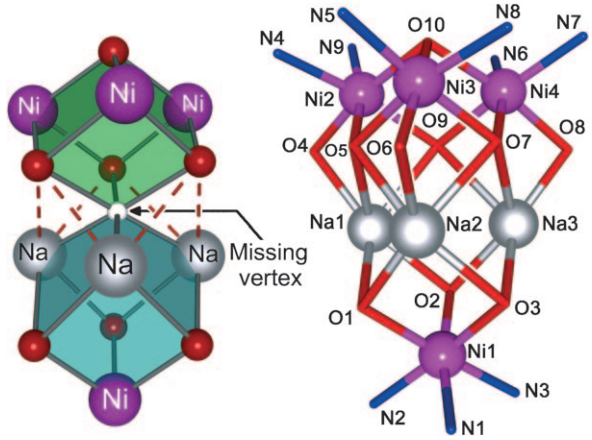

Figure 2. Views of the core atoms of **3**. Left: Two pseudo-cubanes, Ni2, Ni3, Ni4, O5, O7, O9 and Ni1, O1, O2, O3, Na1, Na2, Na3 sharing a missing vertex are highlighted. Color code: N: blue, Na: gray, Ni: violet, O: red.

with NaH, but formation of **3** requires additional NaL, suggesting that the reaction proceeds by attack of L^- on **1**. Decreasing the HL/Ni ratio resulted in the slow formation of the new Ni_7 cluster $[Ni_7L_{12}]Cl_2$ (**4**) (Figure 3).

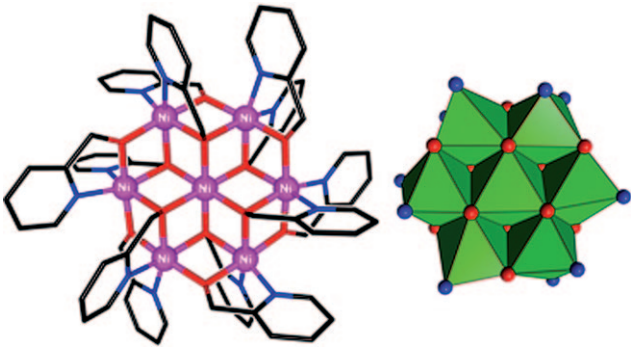

Figure 3. Views of the structure of the Ni_7 cation in $\mathbf{4}\cdot 6CH_2Cl_2\cdot H_2O$. Color code: C: black, N: blue, Ni: violet, O: red. The distorted metal coordination octahedra are shown on the right.

The cation of **4** shows an Anderson-type structure with six face-sharing incomplete cubane moieties arranged in a cyclic manner and seven Ni ions essentially coplanar. Although the $M@M_6$ arrangement is well known in mono-[7] and bimetallic[8] transition-metal oxo complexes, it is new for Ni and has been reported only as a substructure of larger polynuclear Ni complexes,[9] whereas a very similar Zn_7 structure is known.[10] To examine whether this cluster could be transformed into a more common cubane-type complex, an appropriate amount of $[NiCl_2(DME)]$ was added to a solution of **4** in THF (ratio 5:1). This yielded indeed, after crystallization, $[Ni_4L_4Cl_4(H_2O)_4]\cdot THF\cdot H_2O$ ($\mathbf{5}\cdot THF\cdot H_2O$) of approximate S_4 symmetry (see Figure 4 and the Supporting Information). This suggests that other cubane-type clusters may also derive from (overlooked) larger clusters by varying the metal/ligand ratio. The dramatic changes in the nature and structure of the clusters produced upon fine-tuning of the HL/Ni/NaH ratios were further demonstrated when the HL/Ni ratio was set at 2.8:1, a value intermediate between those giving **3** (3.2:1) and **4** (2.2:1). Thus, the new bimetallic cluster $[Ni_6NaL_{12}]Cl$ (**6**) was crystallized as the major product (Figure 5).

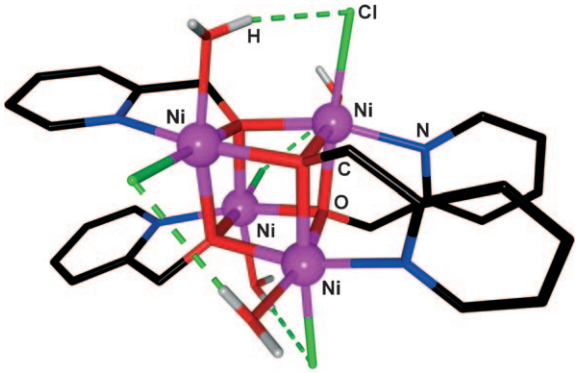

Figure 4. View of the structure of $[Ni_4\{PyCH_2(\mu_3\text{-}O)\}_4(H_2O)_4Cl_4]$ (**5**) in $\mathbf{5}\cdot THF\cdot H_2O$. Color code: C: black, Cl: green, N: blue, Ni: violet, O: red. The structural parameters are consistent with literature data.[11]

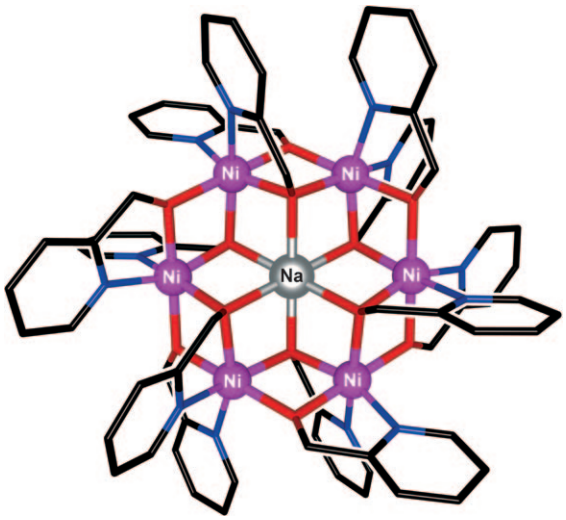

Figure 5. View of the structure of the Ni_6Na cation in **6**. Color code: C: black, N: blue, Na: gray, Ni: violet, O: red.

Monocationic **6** with its central sodium cation is related to dicationic **4** by formal replacement of $NiCl_2$ with NaCl. Although Anderson-type $Na@M_6$ structures are not unusual for transition metals,[12] this arrangement has not been reported before for Ni.

By modifying the L/Ni ratio in these one-pot reactions, one can control the nature and nuclearity of the resulting clusters **3**, **6**, **4**, and **5**, which are characterized by a decreasing L/Ni ratio of 2.25:1, 2:1, 1.71:1 and 1:1, respectively.

Since the magnetic properties of clusters analogous to **5** have been extensively studied,[11a,b,13] we focused our attention on the structurally related **4** and **6**, which feature new topologies for Ni^{II}.

Cluster **4** features both ferromagnetic and antiferromagnetic (J_1 and J_2, respectively, see Figure 6) interactions with a $S=5$ ground state (confirmed by magnetization versus field measurements, see the Supporting Information). The existence of two opposite signs for the J values cannot simply be explained by the variation of the Ni-O-Ni angles, although small changes in the Ni-O-Ni angles around the pivotal value of 100° can inverse the sign of J (antiferromagnetic with angle $>100°$ and vice versa).[15] The Ni(central)-(μ_3-O)-Ni angles range from 95.6(1) to 98.7(1)°, whereas the Ni-(μ-O)-Ni angles are wider, ranging from 102.4(1) to 103.6(1)°. Cluster **6** shows a very weak intramolecular interaction ($J=-0.5\ cm^{-1}$) and this low value may be explained by a specific value of the Ni-O-Ni angles (ranging from 99.2(2)° to 101.4(2)°). Full rationalization of the differences of the coupling constants would be beyond the scope of this study. Thus, clusters **4** and **6** show dramatically different magnetic behaviors related to the presence of different central ions. The magnetic properties of **3** are reported in the Supporting Information.

Oxo-bridged metal clusters are receiving considerable attention owing to their structural diversity and often unique physical properties.[16] We have now found that unusual oxo-bridged Ni clusters can be prepared, in a controlled manner, from readily available reagents. The diversity of compositions and structures results from the remarkable structural effects

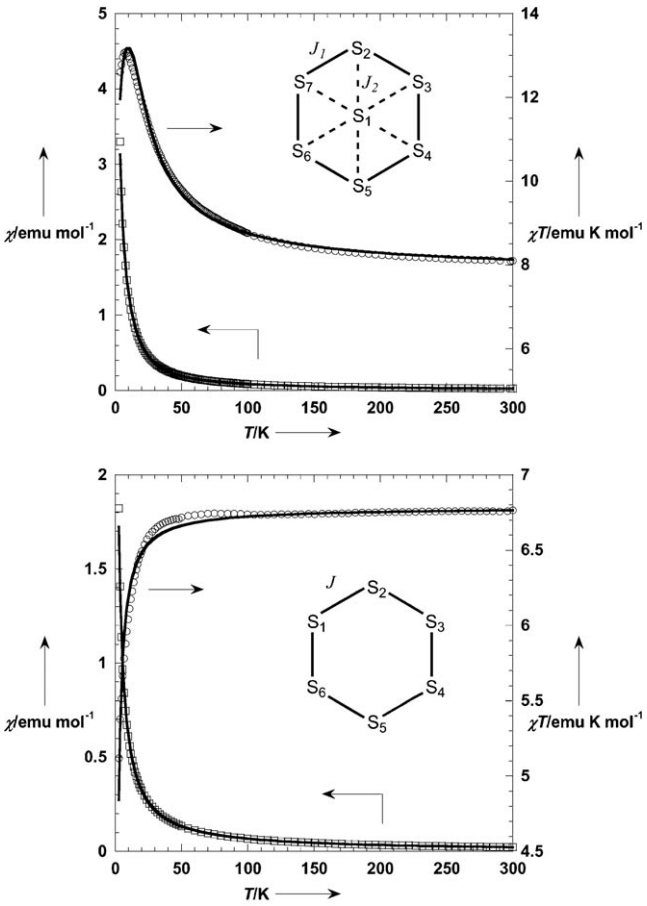

Figure 6. $\chi_M=f(T)$ (squares) and $\chi_MT=f(T)$ (circles) for **4** (top) and **6** (bottom), with the considered spin topology. Full lines correspond to the best fit of χ_MT data.[14] Considering the same g factor and local axial anisotropy parameter for each Ni^{II} ion and assuming each pairwise interaction that can be described in terms of the Heisenberg Hamiltonian of the form $\hat{H}=-J_{ij}\hat{S}_i\hat{S}_j$, the fit led to: for **4**: $g=2.11$, $J_1=12.8\ cm^{-1}$, $J_2=-2.7\ cm^{-1}$ and $|D_{local}|=1.9\ cm^{-1}$ ($R=1.4\times10^{-2}$); for **6**: $g=2.13$ and $J=-0.5\ cm^{-1}$ ($R=9.0\times10^{-3}$) ($R=\Sigma(\chi_MT_{exp}-\chi_MT_{calcd})^2/\Sigma(\chi_MT_{exp})^2$).

of the cations present and subtle changes in the reaction conditions. This work further demonstrates that the cluster self-assembly approach,[17] based on ligands capable of both chelating and bridging transition metals, such as HL, is very powerful because of its versatility and the resulting diversity of structures observed in dinuclear,[18] polynuclear complexes[4,10] and coordination polymers.[5e,19]

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