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Ni^{II}_{20} "Bowls" from the Use of Tridentate Schiff Bases

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Supporting Information

ABSTRACT: The reactions of *N*-salicylidene-*o*-aminophenol or its derivatives and excess of nickel(II) acetate in alcohols have led to Ni^{II}_{20} clusters with an unprecedented "bowl" metal topology.

The current intense interest in the synthesis and study of high-nuclearity molecular 3d metal clusters (or coordination clusters[1]) is driven by a variety of reasons, and potential applications of such species are sought in areas such as high-density data storage,[2] magnetic refrigeration,[3] qubits for quantum computation,[4] and molecular spintronics,[5] among others.

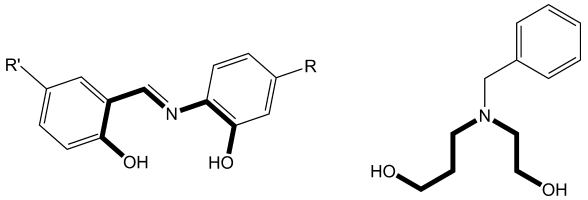
Nickel(II) clusters have been receiving increasing attention in the field of molecular magnetism.[6a] This $3d^8$ metal ion has shown promise in the synthesis of both single-molecule magnets (SMMs)[6b] and spin-phonon traps.[7] These characteristics justify the interest of our group in the chemistry of nickel(II) coordination clusters.[8] One of the ligand families that we have been using in this chemistry derives from the condensation of derivatives of salicylaldehyde with derivatives of *o*-aminophenol (Chart 1, left).

With all of the above in mind, we decided to employ $saphH_2$ and $samphH_2$, *in combination with carboxylate ions* (potentially terminal and/or bridging ligands), in nickel(II) chemistry as a means of obtaining large clusters with exciting structures, uncommon metal topologies, and interesting magnetic properties. The reaction of $Ni(O_2CMe)_2{\cdot}4H_2O$ and $samphH_2$ in a 1:1 molar ratio in methanol (MeOH) gave on orange solution that upon storage at room temperature gave brownish-green dichroic crystals of $[Ni_4(samph)_4(MeOH)_4]{\cdot}0.5MeOH{\cdot}0.4H_2O$ (**1**·$0.5MeOH{\cdot}0.4H_2O$) in ~60% yield. Its molecular structure (Figures S1−S3 in the Supporting Information, SI) is similar to that of $[Ni_4(samph)_4(EtOH)_4]{\cdot}0.7EtOH$ (EtOH = ethanol),[9] consisting of tetranuclear cluster molecules with a cubane $\{Ni_4(\mu_3\text{-}OR)_4\}^{4+}$ core.

The precipitation of *green* crystals from an *orange* reaction solution made us suspect that there was a "hidden" product in the reaction system, possibly with $MeCO_2^-$ as a coligand; we thus increased the $MeCO_2^-/samphH_2$ molar ratio. The reactions of $Ni(O_2CMe)_2{\cdot}4H_2O$ and $samphH_2$ in a 2:1 molar ratio ($MeCO_2^-$:$saphH_2$ = 4:1) in alcohols (MeOH and EtOH) gave dark-orange-red solutions that upon slow diffusion with Et_2O afforded *red* crystals with almost identical IR spectra. The crystals were better from EtOH and were used for single-crystal X-ray analysis to prove that the product (formed in ~70% yield) is $[Ni_{20}(samph)_{12}(O_2CMe)_{16}(EtOH)_{12}]{\cdot}10EtOH{\cdot}1.8H_2O$ (**2**·$10EtOH{\cdot}1.8H_2O$). The $Ni(O_2CMe)_2{\cdot}4H_2O/saphH_2$ chemistry (i.e., that with the parent ligand having R = R′ = H; Chart 1, left) is similar, with the products from EtOH being $[Ni_4(saph)_4(EtOH)_4]$ (**3**) and $[Ni_{20}(saph)_{12}(O_2CMe)_{16}(EtOH)_{12}]{\cdot}5.4EtOH{\cdot}2.2H_2O$ (**4**·$5.4EtOH{\cdot}2.2H_2O$; Figures S4−S9 in the SI).

The saddle-shaped molecule of **2**·$10EtOH{\cdot}1.8H_2O$ (Figure 1) consists of 20 nickel(II) atoms held together by the 24 phenoxide-type oxygen atoms of the 12 doubly deprotonated $\eta^2{:}\eta^1{:}\eta^2{:}\mu_3$-$samph^{2-}$ ligands (Figure S10 in the SI) and 16 oxygen atoms that belong to four $\eta^2{:}\eta^2{:}\mu_4$- and eight $\eta^1{:}\eta^2{:}\mu_3$-$MeCO_2^-$ groups. Peripheral ligation is provided by four $\eta^1{:}\ \eta^2{:}\mu$ $MeCO_2^-$ groups, eight terminally ligated oxygen atoms from the $\eta^1{:}\eta^2{:}\mu_3$ acetates, and 12 EtOH ligands. The core (Figure S11 in the SI) is $\{Ni^{II}_{20}(\mu\text{-}OR)_{24}(\mu\text{-}OR')_{16}\}$, where $2RO^-$ = $samph^{2-}$ and $R'O^-$ = $MeCO_2^-$. The molecule is disposed around a crystallographically imposed S_4 axis, and the asymmetric unit is $\{Ni_5(samph)_3(O_2CMe)_4(EtOH)_3\}$ (Figure S12 in the SI). Each of these Ni_5 units is linked to a neighboring unit through one phenoxide-type oxygen atom (O1) and one oxygen atom (O51) from one $\eta^2{:}\eta^2{:}\mu_4$-$MeCO_2^-$ group, resulting in a Ni^{II}_{20}

Chart 1. Structural Formulas and Abbreviations of the Ligands *N*-Salicylidene-*o*-aminophenol ($saphH_2$), *N*-salicylidene-4-methyl-*o*-aminophenol ($samphH_2$), and 3-[Benzyl(2-hydroxyethyl)amino]-1-propanol (LH_2)[a,11a]



R = H; R' = H ($saphH_2$)
R = Me; R' = H ($samphH_2$)

LH_2

[a]The atoms and bonds in bold emphasize the similarity of the regions that contain the three donor atoms in the two ligand types.

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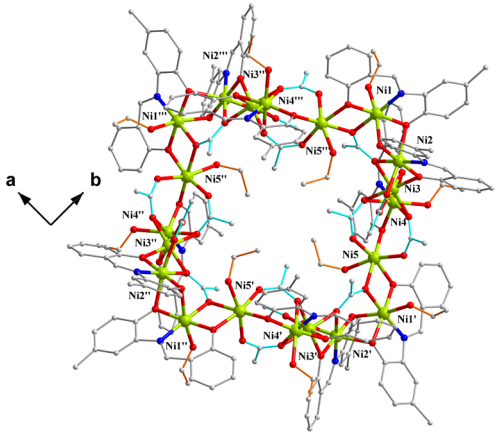


Figure 1. Complete metal-labeled structure of **2**. Symmetry operations: (′) $1.75 - y, -0.25 + x, -0.25 - z$; (″) $2 - x, 1.5 - y, z$; (‴) $0.25 + y, 1.75 - x, -0.25 - z$. Color scheme: Ni^{II}, green; O, red; N, blue; C, gray.

single-stranded loop of S_4 symmetry (Figure S13 in the SI). All nickel(II) atoms are six-coordinate with distorted octahedral geometries; the chromophores are $Ni1O_5N$, $Ni2O_5N$, $Ni3O_6$, $Ni4O_5N$, and $Ni5O_6$. Within each repeating Ni^{II}_5 unit, the five nickel(II) octahedra (Figure S14 in the SI) are linked by sharing edges (Ni1/Ni2 and Ni2/Ni3), faces (Ni3/Ni4), and apexes (Ni4/Ni5). The terminal octahedra of each Ni^{II}_5 unit are each linked to the terminal octahedron of the next S_4-symmetry-related unit by sharing an edge defined by atoms O1 and O51 (or symmetry equivalents).

Compounds **2** and **4** are among the highest-nuclearity, non-organometallic nickel(II) clusters prepared to date,[10] with the record being a Ni^{II}_{26} complex reported recently.[10c] From the Ni^{II}_{20} clusters,[11] complex $[Ni_{20}L_4(LH)_4(O_2CMe)_{28}]$ (**5**),[11a] where LH_2 is the unsymmetrical ligand shown in Chart 1, is worth mentioning. Ligands $saphH_2$/$samphH_2$ and LH_2 are *simultaneously* similar and different. The ligands are similar because they have comparable regions containing the three donor atoms with unsymmetrical (four and three bonds) substituent/donor arms on the central nitrogen atom; this similarity is emphasized in Chart 1. The ligands are different because LH_2 has three different arms (two with donor atoms), whereas $saphH_2$/$samphH_2$ has two substituents attached to the nitrogen atom because of the Schiff base linkage; thus, the two ligand types have different steric and electronic properties. The similarity is reflected in the fact that both ligand types form Ni^{II}_{20} clusters with a saddle-shaped conformation and S_4 symmetry (crystallographic or virtual). The differences between the two types of ligands are reflected in the different cluster stoichiometries and the different metal topologies (Figures 2 and S15 in the SI). Clusters **2** and **4** can be considered as simple "bowls", while **5** as a "bowl with handles and feet".

Solid-state direct-current magnetic susceptibility (χ_M) data on powdered samples of complexes **1**, **2**, and **4** were collected in the 0.3 T (300−30 K) and 0.02 T (30−2.0 K) fields and are plotted as $\chi_M T$ versus T in Figure S16 in the SI. The values of the $\chi_M T$ product at 300 K are 23.62 (**4**·$2H_2O$) and 23.77 (**2**·$2H_2O$) cm^3 K mol^{-1}, respectively, slightly higher than the value of 23.00 cm^3 K mol^{-1} (calculated with $g = 2.15$) expected for 20 noninteracting nickel(II) ($S = 1$) atoms. The values of the $\chi_M T$ product remain essentially constant in the 300−125 K region for both complexes and then increase to values of 50.2 (**2**·$2H_2O$) and 30.6 (**4**·$2H_2O$) cm^3 K mol^{-1} at 6.5 and 15.0 K, respectively, before dropping slightly (**2**·$2H_2O$) and strongly (**4**·$2H_2O$) to values of 44.7 and

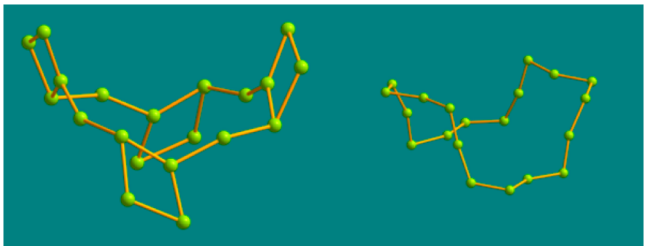
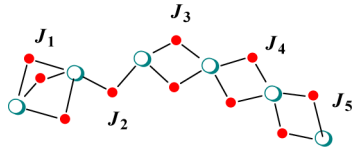


Figure 2. "bowl" (right, complexes **2** and **4**) and "bowl with handles and feet" (left, complex **5**, a type of the Ancient Greek *κύλιξ*) descriptions of the metal topologies in complexes **2**, **4** (present work), and **5**.[11a]

14.8 cm^3 K mol^{-1} at 2.0 K, respectively. The shapes of the curves suggest that both ferro- and antiferromagnetic exchange interactions are present in the Ni_{20} clusters. Low-T $\chi_M T$ values for **2**·$2H_2O$ are field-dependent and thus mainly attributable to D effects, whereas the corresponding values for **4**·$2H_2O$ are field-independent and then probably induced by intercluster interactions. This assumption is reinforced by the field dependence of the magnetization at 2.0 K (Figure S17 in the SI); the magnetization reaches similar values under high fields for both clusters but much more slowly for **4**·$2H_2O$. Thus, compound **2** is a more reliable candidate to try to determine the spin ground state of the cluster and the interaction pattern.

In order to provide a qualitative explanation of the magnetic properties of **2**, we assume as main interactions those provided by the monatomic oxygen bridges under S_4 symmetry, which lead to the repetition of a {−Ni-$(O)_3$-Ni-(O)-Ni-$(O)_2$-Ni-$(O)_2$-Ni-$(O)_2$−} fragment with only five interactions (Chart 2), which can be easily analyzed based on well-established magneto-structural correlations in nickel(II) complexes.[12]

Chart 2. Simplified Coupling Scheme for the Repeating Unit of Cluster 2[a]



[a]From left to right, the nickel(II) centers of the real structure are Ni3, Ni4, Ni5, Ni1′, Ni2′, and Ni3′ (Figure 1).

The triple and double oxygen bridges, which mediate the J_1 and J_4 $Ni^{II}\cdots Ni^{II}$ interactions in **2**, have mean Ni−O−Ni angles of 85.8° and 92.2°, respectively; such interactions are expected to be ferromagnetic (F). In contrast, the single Ni−O−Ni bridge (angle 113.1° and interaction J_2) and the double Ni−$(O)_2$−Ni bridge (angles 102.3° and 95.0°), which mediates J_3 can be clearly associated with antiferromagnetic (AF) coupling. J_5 corresponds to a double bridge with Ni−O−Ni angles (93.1° and 98.4°) near the AF/F switch. The sign of J_5 has a dramatic effect on the spin ground state. We propose that this interaction is F (Table S2 in the SI), and thus the molecule has a $S = 12$ ground state (Figure 3). An AF J_5 interaction would lead to a diamagnetic ($S = 0$) ground state, fully inconsistent with the low-T $\chi_M T$ value. The isothermal magnetization measurement of **2** at 2 K (Figure S17 in the SI) is compatible with a $S = 12$ ground state in the light of its fast increase up to an equivalent value of 20 electrons under an external field lower than 1 T and the continuous increase up to the maximum field, which should be the result of the population of close excited states with $S > 12$. Reduced magnetization data

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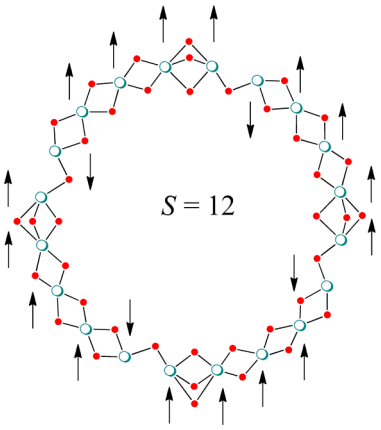

Figure 3. Proposed spin alignment for the Ni_{20} "bowl" of complex **2** according to the F/AF/AF/F/F sequence of the $J_1/J_2/J_3/J_4/J_5$ interactions.

provide evidence for an anisotropic response (Figure S18 in the SI), but as could be expected, the mixing of spin states precludes us from obtaining a reliable fit for the calculation of *D*. Out-of-phase alternating-current susceptibility signals were not observed down to 2 K.

The combined results described herein demonstrate the usefulness of $saphH_2$ and $samphH_2$ to give interesting new high-nuclearity clusters with a novel metal topology and nanoscale dimensions (the largest dimension of the molecule is ∼3 nm) and shows that the presence or absence of carboxylates in the products can have a marked effect on the obtained complexes. Ongoing studies show that the reactions of nickel(II) (and other divalent 3d metals) with $saphH_2$ and $samphH_2$ in the presence of various ancillary ligands (including N_3^- groups) can lead to compounds with unusual structural types and interesting magnetic properties. Results at the time of writing reveal that slight changes in the crystallization procedure that gives **2** lead to similar Ni_{20} clusters, e.g., **6** (Figures S20−S22 in the SI), which crystallize in different space groups and have structures with slightly different topologies compared with that of **2**.

■ ASSOCIATED CONTENT

Supporting Information

CIFs files for complexes **1** and **2** and experimental synthetic details and various structural and magnetism plots for **1**−**6**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00521.

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Notes

The authors declare no competing financial interest.

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