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Rare nuclearities in Ni(II) cluster chemistry: A Ni_{11} cage from the first use of *N*-salicylidene-2-amino-5-chlorobenzoic acid in metal cluster chemistry†

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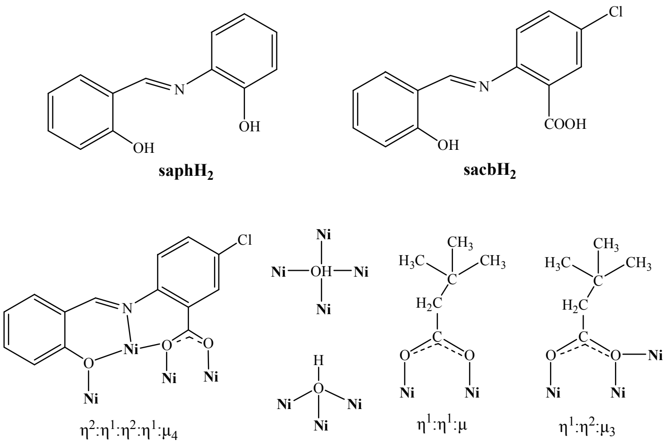
The reaction between *N*-salicylidene-2-amino-5-chlorobenzoic acid (sacbH$_2$), Bu^{t}CH$_2$CO$_2$H, and Ni(ClO$_4$)$_2$·6H$_2$O leads to a new Ni$_{11}$ cluster comprising Ni$_4$ squares and Ni$_3$ triangles; the compound is antiferromagnetically-coupled with an *S* = 1 spin ground state and low-lying excited states populated even at the lowest accessible temperatures.

There are various reasons for the current interest by many groups around the world in the synthesis and study of high nuclearity 3d molecular metal clusters with primarily oxygen-and/or nitrogen-based ligation.[1] Among these is the search for various nuclearity oxido-bridged metal carboxylate clusters to model M_x sites in biomolecules,[2,3] and the modeling of the Ni_2 active site within the metalloenzyme urease which catalyzes the hydrolysis of urea to ammonia and carbamate.[4] Other reasons for this interest are varied, and include the beautiful structures that many such molecular clusters with rare nuclearities possess[5] and the search for compounds with interesting magnetic properties, such as single-molecule magnetism[6] and magnetic refrigeration.[7] Single-molecule magnets (SMMs) are discrete molecules with an appreciable ground state spin value, *S*, and an Ising (or easy-axis) type of magnetoanisotropy that exhibit slow relaxation of the magnetization at low temperatures.[8] They thus represent a molecular, or “bottom-up” approach to nanoscale magnetism with several potential applications in the fields of information storage, molecular electronics and spintronics.[9]

An important factor in the construction of new coordination clusters is the choice of the primary organic bridging/chelating ligand, since this often dictates not only the topology and the number of paramagnetic metal ions present, but also the nature of the intramolecular magnetic exchange interactions.[10] Thus, the use of new or less developed ligands, or a combination of ligands, remains important in the field. Most 3d metal clusters reported to date have been obtained by utilizing the so-called serendipitous assembly, where simple metal salts or preformed small clusters react with multitopic ligands under a variety of conditions.[11] A family of such multidentate chelating/bridging organic ligands is Schiff bases, and particularly the ones which are based on the scaffold of *N*-salicylidene-*o*-aminophenol (saphH$_2$, Scheme 1). The latter is a well-explored precursor in coordination chemistry because of the ability of the relatively soft N atom and the two hard, upon deprotonation, O atoms to bind to a single or multiple metal centers.[12] We have recently reported the employment of saphH$_2$ in high nuclearity 3d/4f-metal cluster chemistry which has led to $Mn^{III}_4Dy^{III}_5$ and $Mn^{III}_4Dy^{III}_3$ complexes with unique topologies and SMM behaviors.[13]

Since then, we were seeking new routes to polynuclear, homometallic 3d metal complexes with unprecedented structures and potentially interesting magnetic properties.[14] We have thus turned our attention into ring-substituted derivatives of saphH$_2$ with both donor and non-donor groups. We decided to replace the -OH donor group of the *o*-aminophenol moiety with a carboxylate (-COOH) functionality which could potentially coordinate to more metal centers than saphH$_2$ through the two O donor atoms and therefore foster formation of very high nuclearity metal species. In addition, we included a non-donor chloride group in place of a phenyl H atom at the fifth position which could, in principle, differentiate the electronic and steric properties, and hydrogen bonding effects. To our knowledge, the resulting ligand *N*-salicylidene-2-amino-5-chlorobenzoic acid (sacbH$_2$, Scheme 1) has never been previously used in coordination chemistry either at its neutral or deprotonated forms. We have thus undertaken the challenge to employ for a first time sacbH$_2$ in Ni^{II} carboxylate chemistry as a means of obtaining new polynuclear compounds with uncommon nuclearities and interesting magnetic properties. Ni^{II} has shown some promise in the synthesis of both SMMs[15] and spin phonon traps,[16] the former taking advantage of its significant single-ion anisotropy[17] and the latter its paramagnetic nature when confined with a highly symmetric cage.



Scheme 1 (top) Structural formulas and abbreviations of the ligands *N*-salicylidene-*o*-aminophenol (saphH$_2$) and *N*-salicylidene-2-amino-5-chlorobenzoic acid (sacbH$_2$), and (bottom) the crystallographically established coordination modes of all bridging ligands present in complex **1**.

The reaction of $Ni(ClO_4)_2\cdot6H_2O$, sacbH$_2$, $Bu^tCH_2CO_2H$ and NEt_3 in a 2:1:2:6 molar ratio in MeCN gave a yellow-green solution that upon slow evaporation at room temperature gave green crystals of $[Ni_{11}(OH)_4(O_2CCH_2Bu^t)_8(sacb)_5(MeCN)_3(H_2O)]\cdot4.5MeCN\cdot1.5H_2O$ (**1**$\cdot4.5MeCN\cdot1.5H_2O$) in 65% yield.‡ The same product can be also obtained in lower yields (~30-35%) by the reaction of preformed "$Ni(O_2CCH_2Bu^t)_2$" with sacbH$_2$ and NEt_3 in a 2:1:2 molar ratio in MeCN.

Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with the $[Ni_{11}(OH)_4(O_2CCH_2Bu^t)_8(sacb)_5(MeCN)_3(H_2O)]$ molecule in a general position. The cage-like structure of **1** (Fig. 1, top) consists of eleven Ni^{II} atoms held together by two μ_4-OH$^-$ (O4, O5) and two μ_3-OH$^-$ (O6, O7) ions (Scheme 1 and Figure 2), as well as the alkoxido and carboxylate fragments of five, double-deprotonated sacb^{2-} ligands. All sacb^{2-} ions bind in the same $\eta^2:\eta^1:\eta^2:\eta^1:\mu_4$ mode, acting as N,O,O-tridentate chelates to a Ni^{II} center and simultaneously bridging three additional Ni^{II} atoms through the phenolate and carboxylate O atoms (Scheme 1). As expected, the Cl-substituent on the sacb^{2-} groups does not participate in coordination, although it is involved in very weak intermolecular interactions with H atoms of phenyl and *tert*-butyl groups of the coordinated ligands. Peripheral ligation is provided by six $\eta^1:\eta^1:\mu$ and two $\eta^1:\eta^2:\mu_3$ $Bu^tCH_2CO_2^-$ groups (Scheme 1), and three MeCN and one H_2O molecules terminally bound to Ni(1,5,9) and Ni(11), respectively. The space-filling representation (Fig. 1, bottom) shows that **1** has a saddle-shaped or sinusoidal conformation with a diameter of 24.9 Å, defined by the longest H…H distance. It also encapsulates one MeCN and one H_2O solvate molecules which are held via hydrogen bonding interactions; these involve the two μ_3-OH$^-$ (O6, O7) ions, the coordinated H_2O and one carboxylate O-atom (Fig. S1).

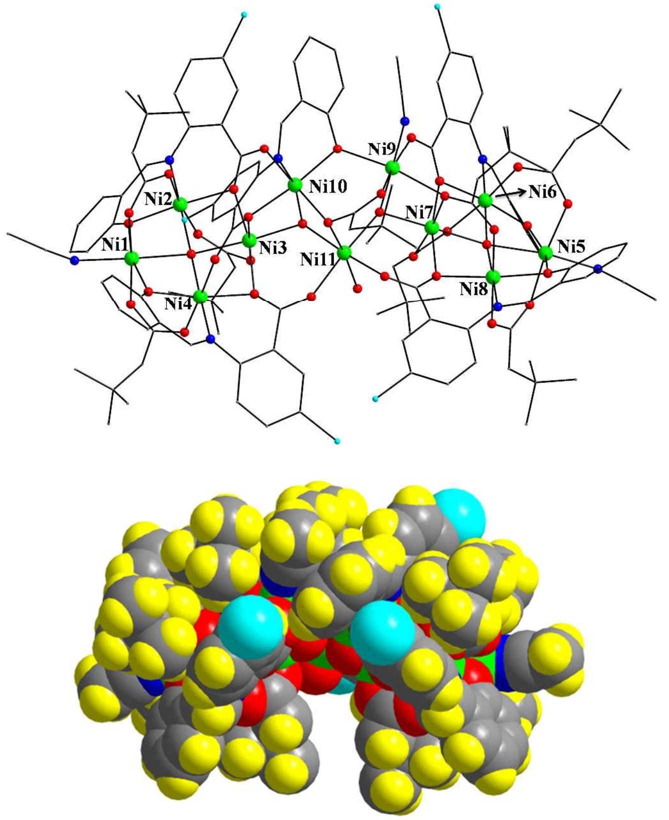


Fig. 1 (top) Partially labeled plot of the Ni$_{11}$ molecule of **1**, with H atoms omitted for clarity. (bottom) Space-filling representation of **1** showing its saddle-shaped conformation. Colour scheme: Ni^{II} green, O red, N blue, Cl cyan, C grey, H yellow.

Thus, complex **1** contains an overall $[Ni_{11}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_2(\mu\text{-}OR)_{12}]^{6+}$ core (Fig. 2), which can be described as two external, almost planar $\{Ni_4(\mu_4\text{-}OH)(\mu\text{-}OR)_4\}^{3+}$ squares [Ni(1,2,3,4) and Ni(5,6,7,8)] at each end, fused to two internal $\{Ni_3(\mu_3\text{-}OH)(\mu\text{-}OR)_2\}^{3+}$ triangles [Ni(3,10,11) and Ni(7,9,11)] which share a common vertex (Ni11) and two edges (Ni10…Ni11 and Ni9…Ni11) with a central Ni$_3$ scalene triangle comprising Ni(9,10,11). The average displacement of the Ni^{II} centers from the mean plane of the Ni(1,2,3,4) and Ni(5,6,7,8) squares is only 0.029 and 0.044 Å, respectively. The μ_4-OH$^-$ groups (O4 and O5) are only slightly displaced out of the Ni$_4$ mean planes by 0.209 and 0.218 Å, respectively. Thus, they have a distorted geometry, close to that of square-planar, which is rare and has been seen only twice before in Ni(II) chemistry.[18] The Ni-(μ_4-OH$^-$)-Ni angles (88.0-92.4º) deviate only slightly from the ideal 90º. The two $\{Ni_3(\mu_3\text{-}OH)(\mu\text{-}OR)_2\}^{3+}$ triangular units are essentially isosceles, the almost equal separations being the Ni3…Ni10, Ni10…Ni11, Ni7…Ni9 and Ni7…Ni11 edges. This is also reflected in the geometry at the μ_3-OH$^-$ ions, O6 and O7, which have a Y-shaped geometry (largest Ni-O-Ni angles of 125.5(2) and 121.0(2)º, respectively) rather than the trigonal planar geometry usually seen in triangular metal carboxylates. The protonation levels of OH$^-$ and H_2O groups were confirmed by oxygen Bond Valence Sum (BVS)[19] calculations which gave values of 1.16 (O4 and O5), 1.10 (O6), 1.13 (O7) and 0.35 (O1W), respectively. Finally, all Ni^{II} atoms are six-coordinate with distorted octahedral geometries.

While the number of polynuclear Ni^{II} complexes continues to grow rapidly, some nuclearities remain rare. Undecanuclear Ni^{II} clusters are particularly rare; **1** belongs to a small family of Ni_{11} clusters reported to date,[20-24] and is the first with such a structural topology. The majority of the previously reported Ni_{11} clusters contain pyridonates as bridging ligands,[21-23] except from the mixed-valence $Ni^{II/III}{}_{11}$ metal chain,[20] a Ni_{11} cluster with metal-metal bonds and a *cyclo*-Ni_{11} cluster.[24]

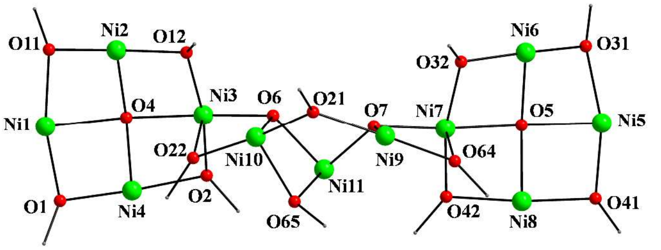


Fig. 2 Labeled representation of the $[Ni_{11}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_2(\mu\text{-}OR)_{12}]^{6+}$ core of **1**. Colour scheme as in Fig. 1.

Variable-temperature direct-current (dc) magnetic susceptibility studies were performed on a powder, crystalline sample of **1**·$3H_2O$ in the temperature range 2.0-300 K in an applied field of 0.3 T. The low-temperature (30-2 K) susceptibility data were re-collected at a very small applied dc field of 0.02 T to avoid saturation effects; these data were identical with the ones collected under 0.3 T, a first indication of a negligible anisotropy in the Ni_{11} system. The data are shown as $\chi_M T$ versus T plot in Fig. 3. The room temperature $\chi_M T$ value is 12.78 cm^3 mol^{-1} K, slightly lower than the spin-only value of 13.31 cm^3 mol^{-1} K with g = 2.2 expected for a cluster of eleven non-interacting S = 1 Ni^{II} atoms. The $\chi_M T$ product for **1**·$3H_2O$ gradually decreases with decreasing temperature in the range 300-25 K, then plateaus to a value of ~4.8 cm^3 mol^{-1} K at 20-10 K, before decreasing more rapidly to a value of 3.67 cm^3 mol^{-1} K at 2.0 K. The shape of the plot indicates an overall antiferromagnetic behavior with different strength of magnetic couplings at different temperature regions, presumably deriving from the different fragments (Ni_4 squares and Ni_3 triangles) of the Ni_{11} cage. The low-temperature (T < 20 K) magnetic susceptibility data suggest a small ground state spin value of S = 1 or 2, either of which could be potentially populated at different (or the same) temperatures (*vide infra*).

Although complex **1** is a very complicated, high-nuclearity and low-symmetry system to rationalize its magnetic behavior, we attempted to interpret and fit the magnetic susceptibility data by finding and inspecting all possible magnetic pathways within the Ni_4 squares and Ni_3 triangles. Close inspection of the metric parameters and structural types of the metal fragments in **1** reveals that there are at least seven different exchange pathways and thus seven different J coupling constants (see inset of Fig. 3). J_1 is associated with the four interactions between the neighboring Ni^{II} centers comprising the edges of the two Ni_4 squares; these are bridged by a doubly (μ-OH^-)/(μ-OR^-) pathway with Ni-O-Ni angles in the range 88.0-96.1° (average value close to 90°). Such interactions are expected to be ferromagnetic.[18] J_2 corresponds to the two next-neighboring interactions between Ni1…Ni3 / Ni2…Ni4 and Ni5…Ni7 / Ni6…Ni8 in the diagonal sites of the Ni_4 squares. These Ni^{II} centers are solely bridged by the central μ_4-OH^- group with the Ni-O-Ni angles spanning the range 165.4-170.8°. Such interactions are expected to be strongly antiferromagnetic,[18] contributing significantly to the high temperature decrease of the $\chi_M T$ product and leading to a local S = 0 spin state for the two Ni_4 squares.

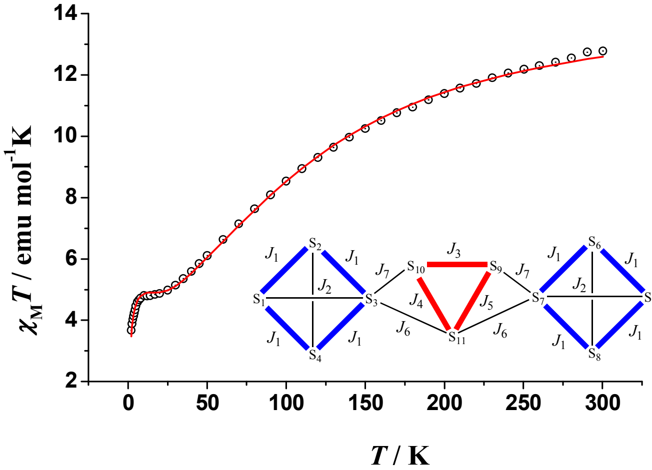


Fig. 3 Plot of $\chi_M T$ *versus* T for complex **1**·$3H_2O$. The solid red line is the fit of the data; see the text for the fit parameters. (inset) definition of the exchange parameters.

The magnetostructural correlations within the Ni_3 triangles [Ni(3,10,11), Ni(7,9,11) and Ni(9,10,11)] were expected to be much more complicated due to the possible presence of competing exchange interactions of similar strengths resulting from the different magnetic pathways.[25] Thus, it became difficult to decrease the number of J coupling constants (in order to avoid overparametarization problems) by making assumptions which could lead to inaccurate and superficial results. Consequently, J_3, J_4 and J_5 are associated with the three different interactions in the central, scalene triangle (Ni9…Ni10 = 3.558 Å, Ni10…Ni11 = 3.072 Å and Ni9…Ni11 = 3.544 Å), arising from the (μ-OR^-), (μ-OH^-)/(μ-OR^-) and (μ-OH^-) bridging scheme, respectively. Similarly, J_6 and J_7 stand for the Ni3…Ni11 / Ni7…Ni11 and Ni3…Ni10 / Ni7…Ni9 interactions, within the two fused to the external Ni_4 squares triangles, through a (μ-OH^-) and a doubly (μ-OH^-)/(μ-OR^-) bridging scheme, respectively. The J_3-J_7 superexchange pathways are expected to contribute to the intermediate-to-low temperature region (<20 K) of the $\chi_M T$ versus T plot of **1** and they can be moderate-to-weak ferro- or antiferromagnetic.

The spin Hamiltonian for such a system, illustrated in the inset of Fig. 3, is given by Eq. (1). An excellent fit of the experimental data (for the entire temperature region) with the program PHI ($H = -2J_{ij}\hat{S}_i \cdot \hat{S}_j$ convention),[26] applying the below Hamiltonian, gave as best-fit parameters $J_1 = 8.4$ cm^{-1}, $J_2 = -38.5$ cm^{-1}, $J_3 = 6.7$ cm^{-1}, $J_4 = 0.2$ cm^{-1}, $J_5 = -0.6$ cm^{-1}, $J_6 = 0.1$ cm^{-1}, $J_7 = 0.9$ cm^{-1}, and $g = 2.29$.

$$H = -2J_1(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3 + \hat{S}_3\cdot\hat{S}_4 + \hat{S}_4\cdot\hat{S}_1 + \hat{S}_5\cdot\hat{S}_6 + \hat{S}_6\cdot\hat{S}_7 + \hat{S}_7\cdot\hat{S}_8 + \hat{S}_8\cdot\hat{S}_5) - 2J_2(\hat{S}_1\cdot\hat{S}_3 + \hat{S}_2\cdot\hat{S}_4 + \hat{S}_5\cdot\hat{S}_7 + \hat{S}_6\cdot\hat{S}_8) - 2J_3(\hat{S}_9\cdot\hat{S}_{10}) - 2J_4(\hat{S}_{10}\cdot\hat{S}_{11}) - 2J_5(\hat{S}_9\cdot\hat{S}_{11}) - 2J_6(\hat{S}_3\cdot\hat{S}_{11} + \hat{S}_7\cdot\hat{S}_{11}) - 2J_7(\hat{S}_3\cdot\hat{S}_{10} + \hat{S}_7\cdot\hat{S}_9) \qquad \text{Eq. (1)}$$

The obtained J_1 and J_2 values are in satisfactory agreement with the moderate ferromagnetic and strong antiferromagnetic exchange coupling constants, respectively, found for other discrete Ni_4 square complexes containing the $\{Ni_4(\mu_4\text{-}OH)(\mu\text{-}OR)_4\}^{3+}$ core.[18] J_3 is found to be moderately ferromagnetic as a result of the single phenoxo bridge (linking Ni9 and Ni10), which is known to induce ferro- or antiferromagnetic interactions depending on small variations into the nature of the Ni_2 pairwise unit.[27a] The remaining J_4-J_7 coupling constants are weak and lying in the borderline of ferro-/antiferromagnetic interactions. This is due to the wide range of different Ni-O-Ni angles (spanning the range 93.6-125.4°) and countercomplementary effects promoted by the copresence of carboxylate and alkoxido bridging groups within the various Ni_2 subunits.[27b] The energies resulted from Eq. (1) revealed a very interesting feature which explains the low-temperature magnetic profile of complex **1**. Three well-isolated spin states, namely the $S = 1$, 2 and 3, are populated at 2 K; $S = 1$ is the lowest lying spin state (population: 59.6%), with the first $S = 2$ excited state lying only 0.9 cm^{-1} above the $S = 1$ level (population: 30.3%) and the second, $S = 3$, excited state lying 2.5 cm^{-1} above the $S = 1$ spin state (population: 10.1%). Thus, the plateau of $\chi_M T$ at ~4.8 cm^3 mol^{-1} K, which does not agree with a well-isolated $S = 1$, 2 or 3 ground state spin value, corresponds to the simultaneous population of these quasi degenerate spin levels (mixture of spin states). The very low temperature (10-2 K) decay agrees with the population of the lowest in energy, $S = 1$ ground state for **1**. We should point out that the J_3, J_4 and J_5 coupling constants cannot be joined into a single J value (i.e., treating the central Ni_3 triangle as magnetically equilateral) because the ground state of the system would be the $S = 0$, in contrast to the experimental findings. However, in an attempt to decrease the number of J constants we joined J_6 and J_7 within the Ni(3,10,11) and Ni(7,9,11) triangles and we obtained a similar quality fit with $J_6 = J_7 = 0.5$ cm^{-1}.

The magnetization *versus* field measurements (Fig. S3) at 2 K show a continuous increase of M as the field increases to a value of ~6 $N\mu_B$ at 5 T, which corresponds to 6 e^- arising from the population of the $S = 3$ spin state. Finally, complex **1** does not exhibit out-of-phase (imaginary) ac magnetic susceptibility signals down to 1.8 K, suggesting this is not a SMM.

The photoluminescence studies of complex **1** were also pursued in both solid state and solution, but unfortunately no emission was detected. This is most likely due to the quenching of the emissive organic sacbH_2 (Fig. S4) by the paramagnetic Ni^{II} centers. Elucidation of the optical behavior of sacbH_2-based complexes shall come of the synthesis of the analogues Zn^{II} clusters albeit this is a difficult task which we are currently working at.

Conclusions

We have shown that the first use of *N*-salicylidene-2-amino-5-chlorobenzoic acid (sacbH_2) in 3d-metal cluster chemistry has afforded a new undecametallic Ni^{II} compound with a cage-like topology and a rare nuclearity. The obtained $[Ni_{11}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_2(\mu\text{-}OR)_{12}]^{6+}$ core of **1** comprises two external, almost planar Ni_4 squares fused to three internal Ni_3 triangles which are vertex- and edge-shared with each other. The combine results demonstrate the ability of the doubly deprotonated form of sacbH_2 to form Ni^{II} clusters with unprecedented motifs and structural conformations distinctly different than the ones seen before from the parent saphH_2 ligand. The magnetic properties of the reported Ni_{11} complex revealed predominant antiferromagnetic exchange interactions, leading to an $S = 1$ ground state with close in energy, low-lying excited states. Ongoing studies show that the reactions of this metal ion (and other divalent 3d metals) with sacbH_2 in the presence of various ancillary ligands can lead to compounds with unusual structural types and interesting magneto-physical properties.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic data (CIF format), synthetic details, and various spectroscopic and magnetism figures for complex **1**. See DOI: 10.1039/c000000x/

‡ Anal. Calcd (Found) for **1**·$3H_2O$: C 46.57 (46.69), H 4.70 (4.82), N 3.50 (3.37). Crystal structure data for **1**·4.5MeCN·$1.5H_2O$: $C_{133}H_{159.5}Ni_{11}N_{12.5}O_{37.5}Cl_5$, M_w=3356.29, monoclinic, space group $P2_1/c$ with a=27.090(3), b=22.251(2), c=28.725(3) Å, β=114.718(4) °, V=15728(3) Å^3, T=150(2) K, Z=4, $R1$ [$I > 2\sigma(I)$]=0.0594, $wR2$=0.1325 (F^2, all data). CCDC 983217.

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GRAPHICAL ABSTRACT

The first use of *N*-salicylidene-2-amino-5-chlorobenzoic acid in metal cluster chemistry has afforded a new Ni^{II}_{11} cage consisting of Ni_4 squares and Ni_3 triangles.