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Structural aesthetics in molecular nanoscience: A unique Ni_{26} cluster with a 'rabbit-face' topology and a discrete Ni_{18} 'molecular chain'

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The use of a previously unexplored Schiff-base ligand in Ni(II) carboxylate chemistry has afforded a Ni_{26} cluster with a record nuclearity that crystallizes with a unique
10 **'rabbit-face'-like topology, and a Ni_{18} compound that adopts an unusual 'molecular chain' structure.**

Polynuclear *3d*-metal complexes with moderate oxidation states, also known as coordination clusters, are high-nuclearity molecular species which do not involve metal-
15 metal bonding but instead, are assembled from multidentate N- and/or O-donor bridging/chelating ligands.[1] The nuclearity of a metal cluster is associated with its size some of which have nanoscale dimensions. The smallest classical nanoparticles fabricated to-date via the top-down approach are
20 of the same order of magnitude as the largest molecule-based metal clusters synthesized by bottom-up methods.[2] However, the synthesis and crystallization of such species has been always a challenging task for coordination chemists. Christou, Winpenny, Brechin, and others,[3] have shown that *3d*-metal
25 clusters can indeed reach the size regimes of small nanoparticles, and apart from their architectural beauty, they can also exhibit high-spin ground states and/or single-molecule magnetism (SMM).[4] Although very high-nuclearity, *3d*-metal clusters are of precedence, their size limit has
30 definitely not been reached to date and new record nuclearities for a given metal ion await discovery.

One succesful route to *3d*-metal clusters with large dimensionalities has been the employment of polydentate chelating/bridging organic ligands that are able to coordinate
35 to several metal centers and adopt a variety of different binding modes.[3] One such family are the Schiff-base ligands based on the *N*-salicylidene-*o*-aminophenol (saphH₂, Scheme S1) scaffold. Instead of employing the parent saphH₂ ligand in Ni^{II} carboxylate chemistry as a means of assembling new
40 polynuclear compounds with unique structures and interesting magnetic properties, we replaced the -OH donor group of the *o*-aminophenol moiety with a carboxylate functionality which can potentially coordinate to more metal centers than saphH₂ through its two O donor atoms. In addition, we substituted a
45 non-donor chloro substituent in place of a phenyl H atom at the 5-position which could, in principle alter the stereo-electronic properties of the system and disrupt the hydrogen bonding interactions within the crystal lattice. Previously the

resulting ligand *N*-salicylidene-2-amino-5-chlorobenzoic acid
50 (sacbH₂, Scheme S1) has been the focus of limited studies in metal cluster chemistry.[5]

Herein we report two new polynuclear metal complexes with diverse nuclearities that crystallize in unique and beautiful structural topologies. The Ni_{26} compound is the
55 highest nuclearity, non-organometallic Ni^{II} cluster reported in the literature to-date[6] and possesses a 'rabbit-face' structural topology, while the Ni_{18} complex is the longest, discrete open-chain structure known and only the third member of a rare family of high-nuclearity "molecular chains".[7] Reaction of
60 $Ni(ClO_4)_2 \cdot 6H_2O$, sacbH₂, NEt₃, and MeCO₂H in a 2:1:6:2 molar ratio in MeCN/MeOH led to the isolation of single crystals of $(NHEt_3)[Ni_{26}(OH)_4(O_2CMe)_{19}(sald)_2(sacb)_{14}(MeOH)_2(H_2O)_6]$ (**1**) in 20 % yield after approximately one month.† The
65 coordinated salicylaldehyde (sald⁻) anions are presumably derived from the metal-assisted, partial hydrolysis of sacbH₂.[8] The analogous reaction with Bu^{t}CO₂H instead of MeCO₂H afforded single crystals of the octadecanuclear $(H_3O)[Ni_{18}(OH)_7(O_2CBu^t)_8(sacb)_{10}(MeCN)_4(H_2O)_2](ClO_4)_2$
70 (**2**) in 28 % yield after ~3 weeks.†

The formula of **1** was based on metric parameters, charge balance considerations and O BVS[9] calculations. The structure of the anion of **1** (Fig. 1, top) consists of 26 Ni^{II} atoms bridged by four μ_3-OH⁻ ions (BVS 1.11-1.20) and the alkoxido
75 and carboxylate fragments of fourteen, doubly-deprotonated sacb²⁻ ligands, two anionic sald⁻ groups and nineteen acetates. Impressively, sacb²⁻ ions bind in three different modes (Scheme S1); two ligands coordinate in an $\eta^3:\eta^1:\eta^1:\mu_3$ manner, a further two adopt the $\eta^2:\eta^1:\eta^2:\mu_3$ modes, while the remaining
80 ten ligands bind in an $\eta^2:\eta^1:\eta^2:\eta^1:\mu_4$ fashion, acting as O,N,O,O-tetradentate chelates to a Ni^{II} center simultaneously bridging three additional Ni^{II} atoms through the phenolate and both carboxylate O atoms. This emphasizes the binding affinity and rich bridging versatility of the sacb²⁻ ligand. In
85 addition, peripheral ligation is provided by nine $\eta^1:\eta^1:\mu$, eight $\eta^1:\eta^2:\mu_3$ and two $\eta^2:\eta^2:\mu_4$ MeCO₂⁻ groups, two $\eta^1:\eta^1:\mu$ bidentate chelating/bridging sald⁻ ligands, and two MeOH and six H₂O (BVS 0.32-0.35) molecules terminally bound to a total of six Ni^{II} atoms; the two MeOH and one H₂O molecules
90 are disordered over three positions. All of the Ni^{II} atoms are six-coordinate with distorted octahedral geometries (orange
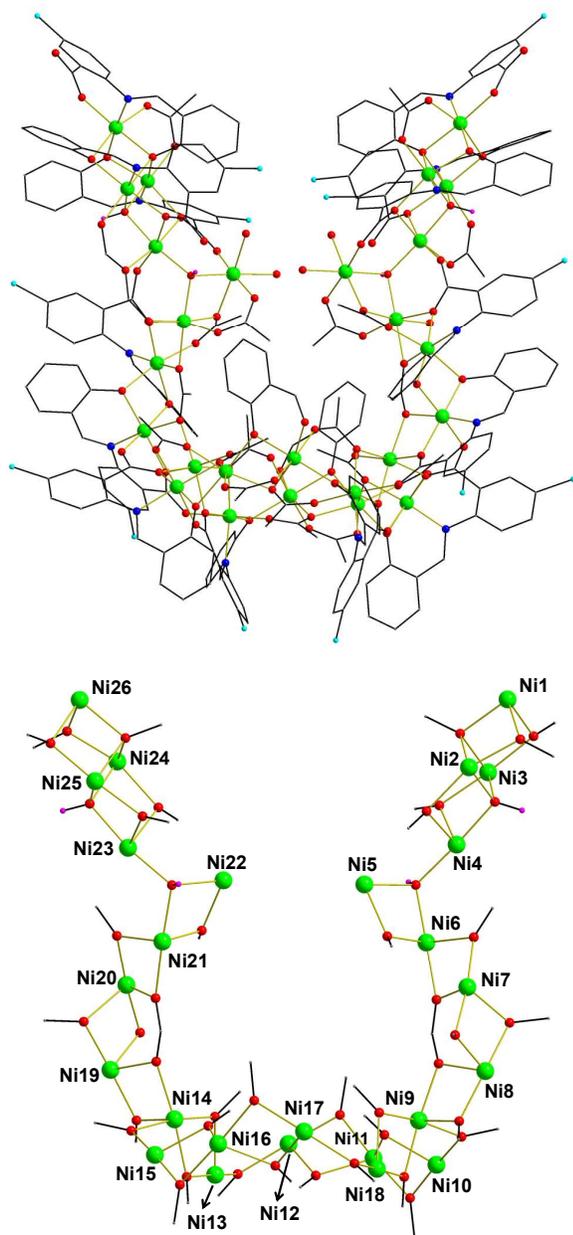
thick bonds in Fig. 1).

Fig. 1 Complete structure of the anion of **1** (top) and its partially-labeled, 'rabbit-face'-like core (bottom). All H atoms except from the ones belonging to the μ_3-OH$^-$ groups are omitted for clarity. Color scheme: Ni^{II} green, O red, N blue, C dark gray, Cl cyan, H purple.

The [Ni$_{26}$(μ_3-OH)$_4$(μ_3-OR)$_2$(μ-OR)$_{38}$]$^{8+}$ core topology of **1** (Fig. 1, bottom) resembles the face of a 'bunny-rabbit' (Fig. S1), with two opposite-side {Ni$_4$(μ_3-OH)(μ_3-OR)(μ-OR)$_4$}$^{2+}$ defective-dicubane subunits as the 'ears' and a central {Ni$_{18}$} unit solely bridged by μ-OR$^-$ groups providing the 'head' (Fig. 2). The {Ni$_{18}$} 'head' can be further divided into two {Ni$_4$} *zig-zag* subunits and a non-planar, 'crown'-like {Ni$_{10}$} moiety with a single-strand wheel topology. Furthermore, the {Ni$_{18}$} subunit is nicely "closed out" by two strong intramolecular H-bonds; these involve the aqua O atoms, O74 and O18, as donors and the carboxylate O atoms, O19 and O72, as acceptors [O74···O19 = 2.77 Å and O18···O72 = 2.73 Å] (Fig.

S2). The space-filling representation (Fig. S3) shows that **1** adopts a saddle-shaped conformation with a diameter of ~24 Å, defined by the longest Cl···Cl distance.
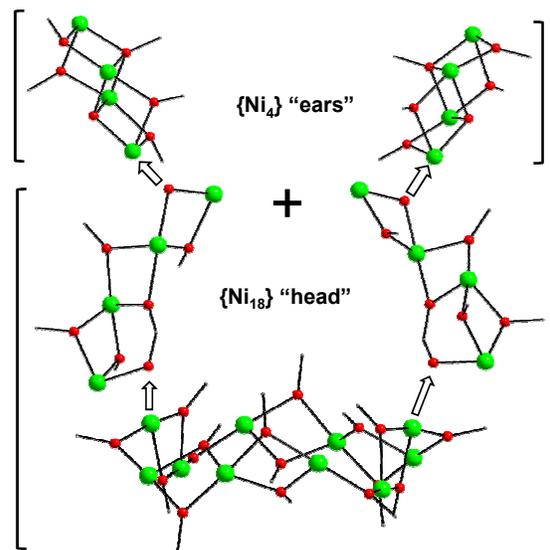

Fig. 2 'Building up' the Ni$_{26}$ core from smaller fragments. The arrows indicate the 'nodal' atoms. Color scheme as in Fig. 1.

Complex **2** crystallizes in the monoclinic space group *C*2/*c* with the asymmetric unit containing a [Ni$_{18}$(OH)$_7$(O$_2$CBu^t)$_8$(sacb)$_{10}$(MeCN)$_4$(H$_2$O)$_2$]$^+$ cation, stabilized by the presence of an H$_3$O$^+$, two ClO$_4^-$ anions, as well as eleven MeCN solvate molecules, all of which are severely disordered.† The formula of the compound was derived based on metric parameters, charge balance considerations and O BVS calculations; the latter confirmed that all bridging, inorganic O atoms belong to OH$^-$ groups. Thus, the charge of Ni$_{18}$ cluster is undoubtedly +1. Given the clear presence of two ClO$_4^-$ counterions in the crystal lattice and the absence of any organic cation to counterbalance the overall -1 charge, we assigned that role to a disordered H$_3$O$^+$ unit located in the crystal lattice. The structure of the centrosymmetric cation of **2** (Fig. 3, top) comprises a remarkable Ni$_{18}$ cluster that can be described as consisting of a consecutive array of Ni$_4$-Ni$_3$-Ni$_4$-Ni$_3$-Ni$_4$ subunits linked into a discrete 'molecular chain' topology (Fig. S4). The eighteen Ni^{II} atoms are held together by three μ_4-OH$^-$ (O51, O51′, O52) and four μ_3-OH$^-$ (O53, O53′, O54, O54′) ions (BVS 1.03-1.18), as well as the alkoxido and carboxylate moieties from ten sacb^{2-} ligands. Eight ligands bind in the common η^2:η^1:η^2:η^1:μ_4 mode and two in the unique η^3:η^1:η^2:η^1:μ_5 fashion, all acting as N,O,O-tridentate chelates to a Ni^{II} center and simultaneously bridging three or four additional Ni^{II} atoms, respectively, through their phenolate and carboxylate O atoms (Scheme S1). Thus, complex **2** possesses a complete [Ni$_{18}$(μ_4-OH)$_3$(μ_3-OH)$_4$(μ_3-OR)$_2$(μ-OR)$_{18}$]$^{9+}$ core (Fig. 3, bottom) with peripheral ligation provided by eight η^1:η^1:μ Bu^{t}CO$_2^-$ groups, four MeCN and two H$_2$O molecules, terminally bound to Ni(4,4′,9,9′) and Ni(4,4′), respectively. The three Ni$_4$ fragments of the 'molecular chain' form similar, near-planar {Ni$_4$(μ_4-OH)(μ-OR)$_4$}$^{3+}$ square topologies. The μ_4-OH$^-$ groups are slightly

displaced out of the Ni$_4$ mean planes by 0.221 and 0.268 Å. The Ni-(μ_4-OH$^-$)-Ni angles span the range 87.9-92.3°, deviating only slightly from ideal 90°. The two, symmetry-related Ni$_3$ fragments adopt a scalene triangular {Ni$_3$(μ_3-OR)(μ-OH)$_2$(μ-OR)}$^{2+}$ motif, with the two edge-bridging μ-OH$^-$ groups becoming μ_3 and linking the Ni$_3$ triangles with adjacent Ni$_4$ squares. Finally, all Ni^{II} atoms are six-coordinate with distorted octahedral geometries. The space-filling representation (Fig. S5) shows that the cation of **2** has a nanotubular structure with a length of ~35 Å, as defined by the longest C···C distance of the externally bound MeCN molecules, and a thickness of ~16 Å as determined by the longest intracluster Cl···Cl separation. Complex **2** is the second Ni$^{II}_{18}$ cluster reported to-date, the first being a planar, disk-like Ni$_{18}$ compound assembled from the hexadentate ligand N-(2-pyridylmethyl)iminodipropionic acid.[10] Thus, the topology of **2** is not only unprecedented in Ni chemistry but it also represents the highest-nuclearity, chain-like metal complex discovered to-date, and can reasonably be called a 'molecular chain'. A 'molecular chain' of the same length, but with Fe^{III} atoms, has been reported by Christou and coworkers,[7a] and consists of an Fe$_{18}$ cluster with a double-headed serpent topology that has an S = 0 spin ground state.
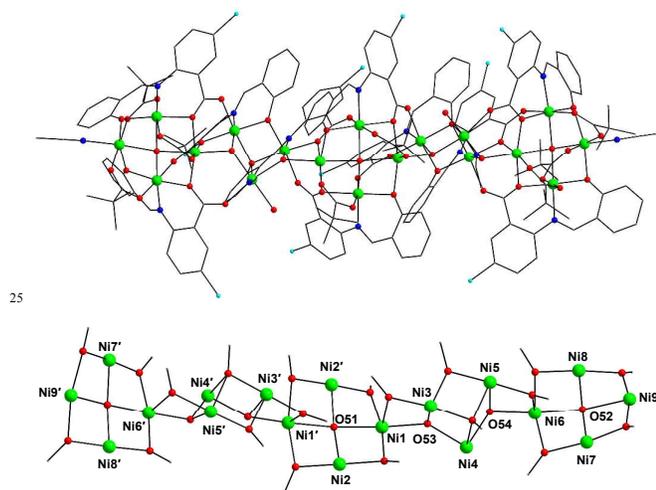

Fig. 3 Complete molecular structure of the cation of **2** (top) and its partially-labeled, 'molecular chain'-like core (bottom). Symmetry operation ('): 2-*x*, *y*, 0.5-*z*. Color scheme as in Fig. 1.

Variable-temperature direct-current (*dc*) magnetic susceptibility measurements were performed on freshly-prepared and analytically-pure (see ESI) microcrystalline solids of **1**·10H$_2$O and **2**·2MeCN in the temperature range 2-300 K; a *dc* field of 0.2 T was applied from 30 to 300 K and a weak *dc* field of 0.02 T was applied from 2 to 30 K to avoid saturation effects. The data are shown as $\chi_M T$ versus *T* plots in Fig. 4. The values of $\chi_M T$ product at 300 K are 31.34 (**1**·10H$_2$O) and 21.36 (**2**·2MeCN) cm^3·mol^{-1}·K, in excellent agreement with the values of 31.46 and 21.78 cm^3·mol^{-1}·K (calculated with g = 2.2) expected for twenty-six and eighteen non-interacting, high-spin Ni^{II} (S = 1) atoms, respectively. For the Ni$_{26}$ complex, the $\chi_M T$ product remains essentially constant in the 300-50 K region and then slightly increases to

a value of 32.20 cm^3·mol^{-1}·K at 35 K, before dropping sharply to a value of 21.25 cm^3·mol^{-1}·K at 2 K. The shape of the curve suggests that both ferro- and antiferromagnetic exchange interactions are likely present within **1**. The $\chi_M T$ value at the lowest temperature and smallest possible *dc* fields suggests a non-zero ground state spin for the complex, with the value at 2 K consistent with an S = 6 or 5 ground state depending on g. Magnetization (M) versus field (H) measurements (Fig. S6) at 2 K show a continuous increase of M as the field increases; this is likely due to the presence of low-lying excited states, as reported previously for other high-nuclearity complexes.[3-7] As a result, attempts to fit the reduced magnetization data assuming that only the ground state was populated were very poor. However, the M versus H plot at 2 K, and for very small fields of < 5000 G, was nicely reproduced upon application of the Brillouin function for an S = 6 ground state with g = 2.2.

In contrast to the magnetic behavior of **1**, the $\chi_M T$ product of Ni$_{18}$ cluster shows a rapid decrease as the temperature is lowered in the range 300-10 K and then a more gradual decrease to a value of 7.33 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 resulting from the different fragments (Ni$_4$ squares and Ni$_3$ triangles) of the Ni$_{18}$ cluster. The continuous increase of magnetization versus field data at 2 K (Fig. S7) supports the presence of low-lying excited states. In order to confirm the ground state S values for **1** and **2**, we carried out alternating-current (*ac*) susceptibility studies, a powerful complement to *dc* studies for determining the S value of a system.[3-7] Extrapolation of the in-phase $\chi_M'T$ data from ~3-10 K to 0 K (Fig. S8) gives values of ~24 and ~10 cm^3·K·mol^{-1}, indicative of S = 6 and S = 4 ground states for **1** and **2**, respectively, with g = ~2.2-2.0. Finally, neither **1** nor **2** exhibit out-of-phase (χ_M'') *ac* signals down to 1.8 K (Fig. S9), suggesting these are not SMMs.
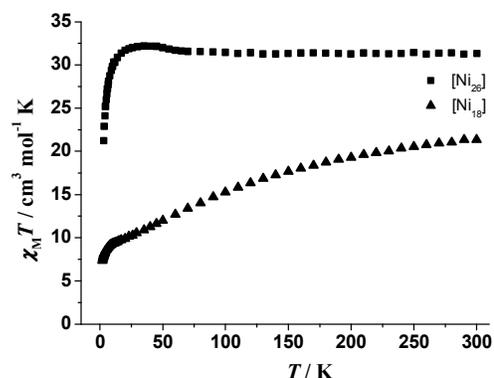

Fig. 4 $\chi_M T$ vs *T* plots for complexes **1**·10H$_2$O (■) and **2**·2MeCN (▲).

In conclusion, we have reported two new novel, diverse molecular clusters with nanoscale dimensions, unprecedented core topologies and record nuclearities. The combined results illustrate the ability of serendipitous assembly to afford interesting nanoscale molecular clusters with sizes similar to the smallest, classical nanoparticles (i.e., metals, metal oxides and alloys). What is really intriguing when comparing the Ni$_{26}$ complex with other examples of high nuclearity homometallic clusters[3-7] is that the majority of these complexes tend to

crystallize in highly-symmetric, closed-shell topologies with wheel-, grid-, or spherical-like structures, one notable exception being the Co_{36} cage reported by Alborés and Rentschler.[3h] There is no explanation *per se* for this trend, or for the exceptions, but it demonstrates that with the appropriate ligand choice and under the right experimental conditions the strategy of self-assembly continues to deliver a diverse range of structurally beautiful topologies that satisfy a broad range of structural tastes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Full synthetic and crystallographic discussion, structural figures, and magnetic data. CCDC-1023378 (**1**), -1023379 (**2**). See DOI: 10.1039/b000000x/

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