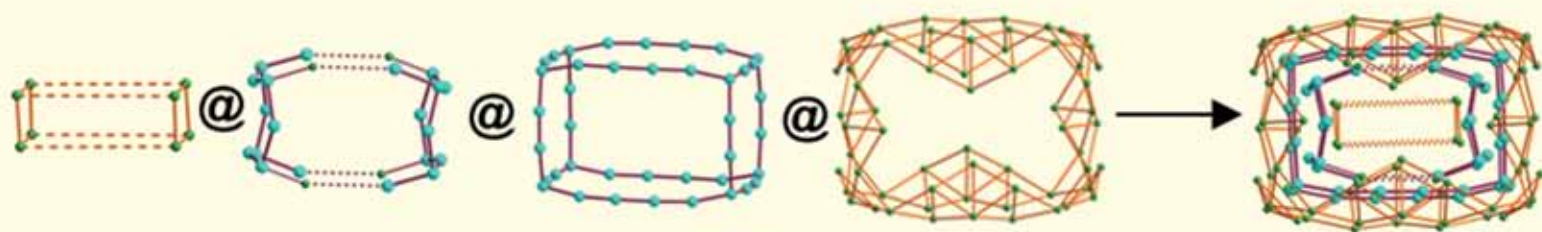


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A four-shell, 136-metal 3d-4f heterometallic cluster approximating a rectangular parallelepiped†

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A nanosized heterometallic cluster containing 60 La(III) and 76 Ni(II) ions, which are arranged into a four-shell, nest-like framework structure, was obtained by the hydrolytic reaction of the mixed La(NO₃)₃–Ni(NO₃)₂ system using iminodiacetate as an ancillary ligand to control the hydrolysis.

High-nuclearity metal clusters that show fascinating structures and interesting properties^{1–11} have attracted continuous attention because of their potential applications in a number of research fields, including physics,² chemistry,³ biology,⁴ nanotechnology⁵ and materials science.⁶ Of particular interest are heterometallic clusters featuring both d- and f-block elements within the cluster core. Apart from their structural appeal, there lies the opportunity of realizing functional materials with properties that are not possible with either their homometallic analogues or their lower-nuclearity cognates.

A great variety of 3d-4f cluster complexes have been reported, of which the few giant ones containing more than one hundred metal ions in their nanosized core structures are most notable.^{7,8} Our own efforts in search for high-nuclearity heterometallic clusters have yielded the double-sphere, sandwich-like Ln₂₀Ni₂₁ (Ln = Nd and Pr) clusters,⁹ a Keplerate-type¹⁰ La₂₀Ni₃₀ cluster,¹¹ and a four-shell, Russian doll-like Gd₅₄Ni₅₄ cluster.¹²

During the course of such studies, the profound influences of the reaction conditions on the identity of the resulting clusters have been realized. For example, under hydrothermal conditions, a mixture of Ln(NO₃)₃ (Ln = Pr, Nd) : Ni(NO₃)₂ : IDA (IDA = iminodiacetate) in a ratio of 2 : 3 : 4 produced the Ln₂₀Ni₂₁-cored (Ln = Pr, Nd) clusters, while under otherwise identical conditions, a mixture with a ratio of 2 : 5 : 4 led to the isolation of 108-metal clusters of the Ln₅₄Ni₅₄ core (Ln = Gd). It appears that an increase in the starting Ni/L or (Ln + Ni)/L ratio favors the formation of higher-nuclearity clusters. However, such conclusion-drawing

is complicated by ligand decomposition under the hydrothermal conditions and the coordination by the resulting small ligands.

Recognizing the aforementioned complications, we have carried out our first study of cluster synthesis under ambient pressure conditions. Very different results have been obtained. We report herein a 136-metal cluster, [La₆₀Ni₇₆(IDA)₆₈(μ₃-OH)₁₅₈(NO₃)₄(H₂O)₄₄](NO₃)₃₄(H₂O)₄₂ (**1**), believed to be the largest member hitherto known of the fascinating 3d-4f cluster family, produced under atmospheric pressure by the hydrolytic reaction of the mixed La(NO₃)₃–Ni(NO₃)₂ system using iminodiacetate as an ancillary ligand for hydrolysis control.†

The structure of the cationic cluster complex, approximating a rectangular parallelepiped, is shown in Fig. 1. It has a dimension of 23 × 23 × 31 Å³. The structure may be

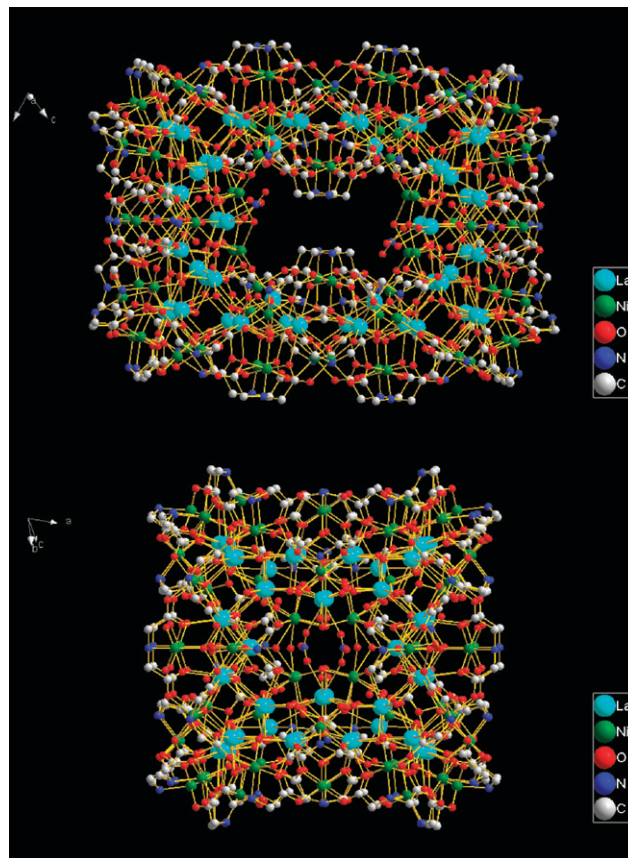


Fig. 1 Ball and stick plot of the cationic cluster complex [La₆₀Ni₇₆(IDA)₆₈(μ₃-OH)₁₅₈(NO₃)₄(H₂O)₄₄]³⁴⁺ along the *bc* plane (top) and the *ac* plane (bottom).

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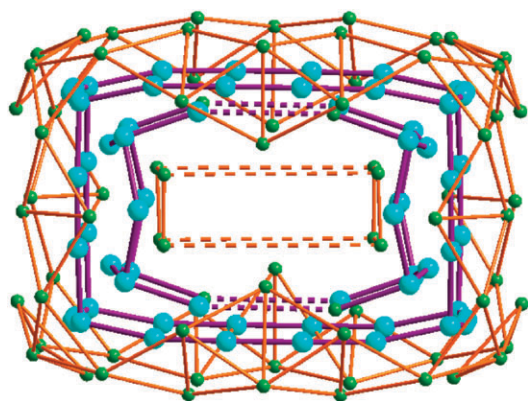


Fig. 2 Ball and stick plot of the $\text{La}_{60}\text{Ni}_{76}$ framework with its four shells distinctly shown.

viewed as an elongation along one of the axes of the cube-shaped $\text{Gd}_{54}\text{Ni}_{54}$ cluster¹² with its 136 metal ions organized in four distinct shells. Moving outward from the innermost shell, 8 Ni(II) ions in Shell 1 are encaged by Shell 2 of $\text{La}_{20}\text{Ni}_4$, followed by Shell 3 of La_{40} and then Shell 4 of Ni_{64} (Fig. 2). Adjacent shells of metals are linked by triply bridging hydroxo groups, forming a brucite-like structure (Fig. 3), similar to some previously reported clusters.¹³

Eight Ni(II) ions form the core structure of Shell 1. The two opposite faces of the rectangular parallelepiped along the longer edge are at a distance of 11.6 Å. The Ni(II) ion is pentacoordinate, exclusively with triply bridging hydroxo groups that also bridge neighboring Ni(II) ions within the same shell and La(III) and Ni(II) ions in Shell 2.

Shell 2 of $\text{La}_{20}\text{Ni}_4$ has a size of $7.8 \times 7.8 \times 15.3$ Å (Fig. 2). The two opposite faces of the rectangular parallelepiped, consisting of 8 La(III) ions, may be viewed as a La_4 square with each of its sides bridged by one La(III) ion. Four longer edges, each of which consisting of one Ni(II) and one La(III) ion, connect the opposite faces to complete the core structure. Nine μ_3 -OH groups form the coordination sphere for each of the vertex-occupying La(III) ions while providing connections to neighbouring metal ions within Shell 2 and those in Shells 1 and 3. The edge La(III) ions are also nonacoordinate, featuring six μ_3 -OH groups, one aqua ligand, and one chelating NO_3^- . The La(III) ions present in the longer edge have a coordination number of 8, with contributions from 3 μ_3 -OH groups, one

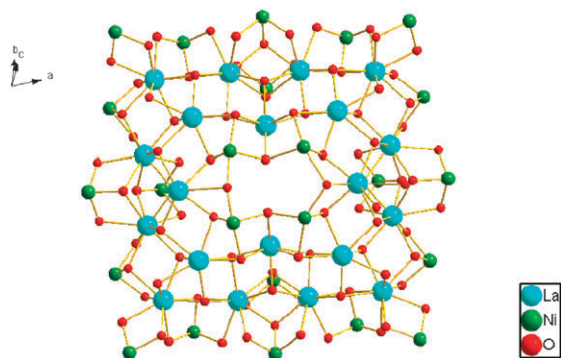


Fig. 3 Ball and stick plot showing the brucite-like cluster core structure.

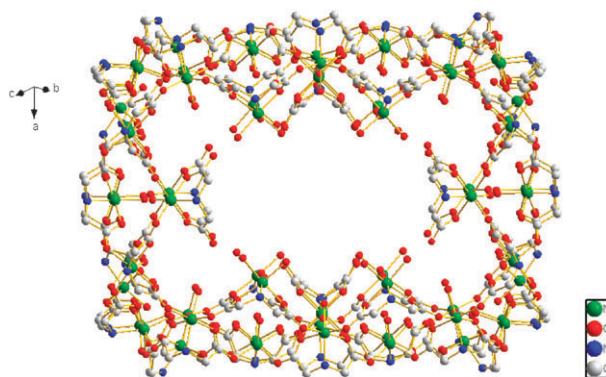


Fig. 4 Ball and stick plot of Shell 4, the outmost framework of $[\text{Ni}_{64}(\text{IDA})_{64}]$.

H_2O , and two IDA ligands. The Ni(II) ion in the four longer edges are each tetracoordinate, with 3 μ_3 -OH groups and one IDA carboxylate O atom.

Shell 3 contains 40 La(III) ions and can be viewed as a rectangular parallelepiped with a dimension of $12.0 \times 12.0 \times 19.8$ Å³. The 40 La(III) ions are of three different types in terms of their coordination environments, the 8 vertex La(III) ions (Group 1), the 24 La(III) ions adjacent to the vertices (Group 2), and the remaining 8 that are remote from the vertices in the longer edges (Group 3). Each of the La(III) ions in Group 1 connects one La(III) ion in Shell 2, 3 La(III) ions in Shell 3, and 3 Ni(II) ions in Shell 4 using 6 μ_3 -OH groups and 3 carboxylate O atoms from different IDA ligands. Each of the Group 2 La(III) ions is coordinated by 6 μ_3 -OH and 3 carboxylate O atoms, while Group 3 La(III) ion is decacoordinate, featuring 5 μ_3 -OH and 5 carboxylate ligands.

The outmost shell of Ni_{64} can be viewed as a truncated rectangular parallelepiped whose vertices are triangles of Ni(II) (Fig. 4). Each of its shorter edges contains two Ni(II) ions whose connection runs perpendicular to the edge itself. The longer edge is occupied by three pairs of Ni(II) ions, whose arrangement can be viewed as two edge-sharing butterfly-shaped Ni_4 units. Some common features are shared by these different types of Ni(II) ions: (1) each Ni(II) ion is situated in a distorted octahedral coordination sphere; (2) adjacent Ni(II) ions are linked by an IDA ligand with its carboxylate bridging the metal ions in an *anti-syn* fashion; (3) each Ni(II) ion is linked to two La(III) ions of Shell 3 *via* one μ_3 -OH and two carboxylate O atoms. The rest of the coordination sphere is fulfilled by two IDA carboxylate O atoms or two aqua ligands. The Ni–O and Ni–N distances are 1.9687(2)–2.1244(3) Å and 2.0525(3)–2.1246(4) Å, respectively, both comparable to corresponding values in other Ni–IDA complexes.¹¹ The shortest separations between neighbouring metal ions, $\text{La}\cdots\text{La}$, $\text{La}\cdots\text{Ni}$, and $\text{Ni}\cdots\text{Ni}$ are 3.6948(5)–4.2065(6) Å, 3.5491(4)–4.2578(7) Å, and 3.7063(5)–5.4853(6) Å, respectively. These values are similar to those found in a related complex recently reported.¹¹

The temperature dependence of the magnetic susceptibility of the title complex was measured from 2 to 300 K in an applied magnetic field of 1000 Oe. Shown in Fig. 5 are the plots of $\chi_{\text{M}}T$ versus T . The $\chi_{\text{M}}T$ value is $75.1 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K, close to the value of $76.0 \text{ cm}^3 \text{ K mol}^{-1}$ calculated for

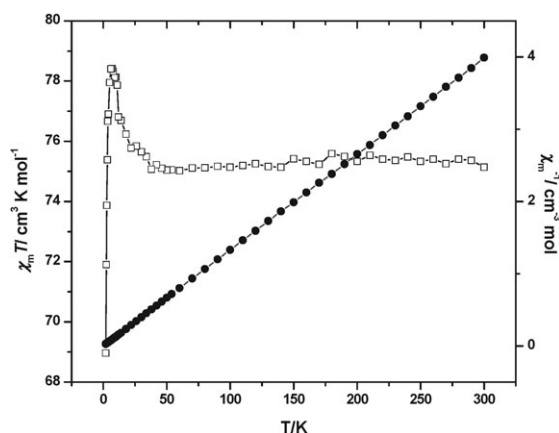


Fig. 5 Plots of temperature dependence of $\chi_M T$ (\square) and χ_M^{-1} (\bullet) for compound **1** between 2 and 300 K.

76 non-interacting Ni(II) ions ($S = 1$, $g = 2$). This value remains essentially constant upon lowering of the temperature until about 38 K when an increase occurs with a maximum of $78.4 \text{ cm}^3 \text{ K mol}^{-1}$ reached at about 7 K. These observations suggest weak ferromagnetic interactions between the Ni(II) ions. Upon further lowering of the temperature, the $\chi_M T$ value drops abruptly to $69.0 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. This may be rationalized as inter-cluster antiferromagnetic interactions at this temperature.¹⁴ The data in the range of 7–300 K can be fitted to the Curie–Weiss law with $C = 72.5 \text{ cm}^3 \text{ K mol}^{-1}$ and $\Theta = 0.06 \text{ K}$; the near-zero Θ value indicates that this cluster complex is essentially paramagnetic in this temperature range.

In summary, the synthesis, structural characterization, and magnetic studies of a giant heterometallic 3d-4f cluster containing 60 La(III) and 76 Ni(II) ions are reported. The metal ions are arranged into four distinct shells, forming a structure approximating a rectangular parallelepiped. Intershell connections are provided by triply bridging hydroxo groups and chelating/bridging iminodiacetate ligands. Magnetic studies revealed weak ferromagnetic interactions between the Ni(II) ions.

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Notes and references

† Complex **1** was synthesized as follows: a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.727 g, 2.50 mmol), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.866 g, 2.00 mmol), and iminodiacetic acid (0.266 g, 2.00 mmol) in 15 mL of deionized water was stirred at about 80°C while a freshly prepared NaOH solution (aq. 1.0 M) was added dropwise to the point of incipient but permanent precipitation. The mixture was then brought to and maintained under reflux for 5 h. The resulting mixture was filtered while hot. Evaporation of the filtrate under ambient conditions afforded

blue block-shaped crystals as the product (yield 35% based on $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Anal. calcd. for $\text{La}_{60}\text{Ni}_{76}\text{C}_{272}\text{H}_{670}\text{N}_{106}\text{O}_{630}$ (FW = 28 303.70): C, 11.54; H, 2.39; N, 5.25. Found: C, 11.55; H, 2.33; N, 5.23%.

Magnetic measurements were carried out with a Quantum Design SQUID MPMS magnetometer working in the 2–300 K range. The magnetic field was 1000 Gauss. Diamagnetic corrections were made with Pascal's constants.

Crystal data for **1**: ($\text{La}_{60}\text{Ni}_{76}\text{C}_{272}\text{H}_{670}\text{N}_{106}\text{O}_{630}$), triclinic, space group $P\bar{1}$ with $a = 27.052(5)$, $b = 30.054(5)$, $c = 33.805(6)$ Å, $V = 22\,742(7)$ Å³, $Z = 1$, $M = 28\,303.70$; 162 326 reflections, with 79 330 unique and 48 256 with $I > 2\sigma(I)$, collected on Bruker SMART CCD with monochromatic MoK α radiation ($\lambda = 0.71073$ Å), 2297 parameters (La and Ni: anisotropic; C, N and O: isotropic) and $2.66 < 2\theta < 50$, $R_1 = 0.0602$ [$I > 2\sigma(I)$], $wR_2 = 0.1747$ [all data], $\text{GOF}(F^2) = 1.035$. There are 42 guest water molecules and 34 NO_3^- counter ions per formula unit, as indicated in the difference density map. They are however severely disordered and were therefore removed by SQUEEZE in structural refinement. CCDC 700140.

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