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A Keplerate Magnetic Cluster Featuring an Icosidodecahedron of Ni(II) Ions Encapsulating a Dodecahedron of La(III) Ions

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The last two decades have witnessed a surge of research activities in the exploratory synthesis and property studies of molecular magnetic materials, largely stimulated by their envisioned technological applications.[1] Arguably most notable in this context is the research on polynuclear metal complexes. By design or serendipity, a great variety of polynuclear complexes have been realized, many of which display aesthetically pleasing structures and extraordinary magnetic properties.[2] One particular class of complexes receiving much recent interest in this vein features both *d*- and *f*-block elements within the same complex framework.[3,4] Besides their interesting structures, significant magnetic properties have been demonstrated as a result of the cooperativity between the different metals.[3]

Here we report the synthesis, structural characterization, and magnetic studies of a gigantic mixed metal cluster (**1**) consisting of 20 La(III) and 30 Ni(II) ions. The compound, formulated as $[La_{20}Ni_{30}(IDA)_{30}(CO_3)_6(NO_3)_6(OH)_{30}(H_2O)_{12}](CO_3)_6{\cdot}72H_2O$ (IDA = iminodiacetate; $C_4H_5NO_4$), was synthesized under hydrothermal conditions using a mixture of $Ni(NO_3)_2{\cdot}6H_2O$ (0.436 g, 1.50 mmol), $La(NO_3)_3{\cdot}6H_2O$ (0.433, 1.00 mmol), and iminodiacetic acid (0.266 g, 2.00 mmol) in 15 mL of deionized water. Evaporation of the resulting blue solution under ambient conditions afforded the product as cube-shaped blue crystals in 30.0% yield (Supporting Information).

Figure 1 shows the asymmetric unit of the cationic complex structure, while its highly sophisticated yet stunningly beautiful structure is depicted in Figure 2 (left). The metal cluster core features a fascinating double-sphere structure of the Keplerate type with an outer sphere formed by 30 Ni(II) ions encapsulating the inner sphere of 20 La(III) ions (Figure 2, right). The 30 Ni(II) ions span an icosidodecahedron, one of the Archimedean solids formed by 12 pentagonal and 20 triangular faces, while the 20 La(III) ions occupy the vertices of a perfect dodecahedron, one of the Platonic solids featuring 12 pentagonal faces. The cage-like arrangement of the two distinct sets of metal ions manifests the beauty of symmetry as both ideally possess icosahedral (I_h) symmetry, the highest possible symmetry for molecules.[5] The structural aesthetics is comparable to that of the celebrated nanocapsule of polyoxometalates,[6] the fullerene-like clusters,[7,8] and the Pd_{145} cluster.[9]

The shortest La−La distances range from 4.089 to 4.198 Å (avg. 4.148 Å), while the Ni−Ni counterparts range from 5.144 to 5.451 Å (avg. 5.256 Å). The two metal spheres are linked by bridging IDA ligands and triply bridging μ_3-OH groups. Each Ni(II) ion and its two nearest La(III) neighbors, together with the bridging O atoms, form a core that approximates an incomplete cube.

The metal coordination sphere is completed with additional IDA, bridging aqua ligands, μ_3-OH groups, NO_3^-, and CO_3^{2-}. The CO_3^{2-} is a putative product of IDA decomposition under hydrothermal conditions, for which precedents are known in the literature.[10]

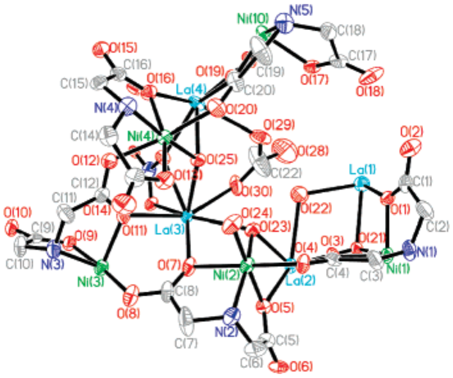

Figure 1. The asymmetric unit of compound **1**, less the counterion CO_3^{2-} and crystallization water.

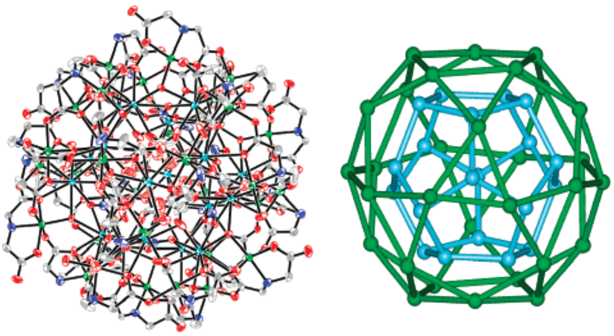

Figure 2. Crystal structure of **1** with H atoms and the counterion CO_3^{2-} removed for clarity (left). The cluster core structure displaying the Ni_{30} icosidodecahedron encapsulating the La_{20} dodecahedron (right). Color legends: Ni (green), La (cyan), O (red), N (blue), C (gray).

The coordination environment of the Ni(II) ions is best described as a distorted octahedron. Despite some subtle differences, certain features are shared by the coordination of the five Ni(II) ions in the asymmetric unit. Each Ni(II) features contribution of three coordinating atoms from an IDA ligand (an N and two O atoms, one from each of its carboxylate groups). For Ni4, these atoms are disposed in a meridional arrangement and one of the carboxylate O of this particular IDA ligand remains uncoordinated. In contrast, the corresponding IDA ligands for the other Ni(II) ions have their three coordinating atoms positioned in the facial configuration, with the two remaining carboxylate O atoms coordinating neighboring Ni(II) ions. Other common features include the occupation of the position *trans* to the IDA N atom by a μ_3-OH group. The rest of the coordination sphere is fulfilled either by two IDA carboxylate O atoms (for Ni1, Ni3, Ni4, Ni10) or by one carboxylate O atom and a terminal aqua ligand (for Ni2). The average distances of Ni−N (2.079 Å) and Ni−O (IDA, 2.049 Å) are in good agreement with other crystallographically characterized Ni−IDA systems.[11]

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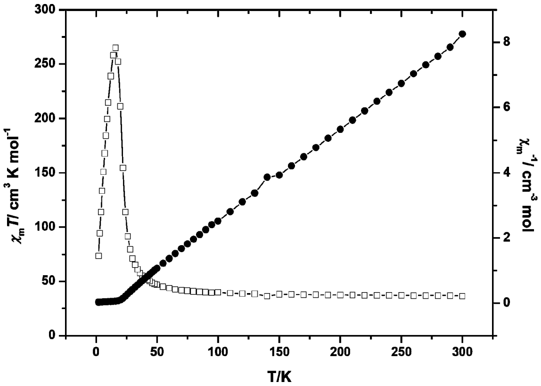

Figure 3. Plots of temperature dependence of $\chi_M T$ (□) and χ_M^{-1} (●) of **1**.

The Ni−O distances (μ_3-OH, 2.036 Å; terminal aqua ligand, 2.072 Å) are also within the ranges expected for such coordination.

The coordination geometry of the La(III) ions is not as well-defined due to flexible coordination of the lanthanides. La2 is decacoordinate, while the other La(III) ions are nonacoordinate. Each of the La atoms features coordination with three μ_3-OH groups in addition to contributions by two (for La3) or three carboxylate oxygen atoms (for La1, La2, La4) of IDA ligands. Furthermore, all La(III) ions except La1 feature coordinating CO_3^{2-} and NO_3^-. For La1 and La2, three and one bridging aqua ligands are seen in their respective coordination sphere. The La−O distances of various kinds (μ_3-OH, bridging H_2O, CO_3^{2-}, NO_3^-, or IDA) are all within the normal ranges.[12]

Magnetic susceptibilities of **1**, measured in an applied field of 1000 Oe over the temperature range of 2−300 K, are shown in Figure 3 in the form of $\chi_M T$ versus T. The $\chi_M T$ value of 36.34 cm^3 K mol^{-1} at 300 K corresponds to 30 uncorrelated Ni(II) ions with μ_{eff} (per Ni) $= 3.14\ \mu_B$ and $g = 2.22$ (calculated 36.67 cm^3 K mol^{-1}). The susceptibility arises solely from the Ni(II) ($s = 1$) ions that are expected to exhibit spin-only moments modified by the effects of second-order spin−orbit coupling over the temperature range of 34−300 K.[13] Upon lowering the temperature, $\chi_M T$ increases abruptly and reaches a maximum of 264.81 cm^3 K mol^{-1} at 16 K, indicating ferromagnetic interactions between the Ni(II) ions. Upon further lowering the temperature, a sharp drop is seen, and a value of 73.49 cm^3 K mol^{-1} is reached at 2 K, suggesting inter-cluster antiferromagnetic interactions. The temperature dependence of the molar susceptibility is well described by a Curie−Weiss term $\chi = C/(T - \Theta)$ with $C = 35.46$ cm^3 K mol^{-1} (according to 30 $s = 1$ centers with $g = 2.22$) and $\Theta = 10.33$ K, consistent with ferromagnetic coupling between the Ni(II) ions. More in-depth magnetic studies are underway to further elucidate its unique magnetic properties.

The cationic complex constitutes a framework of Ni(II) centers with an unusual spin topology as in the case of the seminal $Mo_{72}Fe_{30}$ cluster.[14] The magnetism of $Mo_{72}Fe_{30}$ can be described using a classical Heisenberg model down to very low temperatures due to the high s values of the Fe(III) centers.[15] However, its VO^{2+} analogue with a spin of $s = {}^1/_2$ has been shown to display significantly different magnetic properties.[16] Compound **1** and its anticipated analogues employing other lanthanide or transition metal ions shall in this context present a perfect system for systematic and comparative studies of classical and quantum magnetism in these magnetic clusters. Moreover, although most of the current work is concerned with the synthesis and property investigation of magnetically cooperating molecules, efforts have been shown to create more sophisticated supramolecular organizations using individual molecules as building blocks.[17] This enables the creation and manipulation of cooperative interactions among individual high ground-state spin complexes in a controlled fashion.[18] Our efforts have already yielded a three-dimensional network featuring the cluster units of **1** interconnected by units of $La(NO_3)_3/NaNO_3$. Preliminary studies have shown rather different magnetic properties from those of **1** (Supporting Information). Considering the rich variety of metals as well as the anticipated ready extension of the synthetic methodology, opportunities abound for the preparation and property investigation of these novel nanoscopic magnetic clusters.

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Supporting Information Available: Details of synthesis and crystallographic data of **1**, magnetic studies of **1**, and the network based on linked units of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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