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Short communication

Two nanosized cage-like $Ln_{20}Ni_{21}$ clusters exhibiting antiferromagnetic properties

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ABSTRACT

Two novel nanosized polynuclear cage-like clusters, formulated as $[Nd_{20}Ni_{21}(IDA)_{21}(NH_2CH_2COO)_6(OAc)_3(CO_3)_6(C_2O_4)_3(\mu_3\text{-}O)_9(\mu_3\text{-}OH)_{12}(\mu_2\text{-}OH)_3\cdot 12H_2O]\cdot 32H_2O$ (1), and $[Na_3Pr_{20}Ni_{21}(IDA)_{21}(NH_2CH_2COO)_6(OAc)_9(CO_3)_6(C_2O_4)_3(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_{15}(\mu_2\text{-}OH)_3\cdot 12H_2O]\cdot 15H_2O$ (2) (IDA = iminodiacetic acid), were successfully synthesized under solvothermal conditions by using the flexible ligand IDA. Compounds **1** and **2** are analogous and contain $[Ln_{20}Ni_{21}]$ units connected by IDA, CO_3^{2-}, $NH_2CH_2COO^-$ and $C_2O_4^{2-}$. In addition, magnetic properties of compounds **1** and **2** reveal the existence of antiferromagnetic exchange interaction between adjacent metal ions.

Retrospectively, the synthesis of nanosized polynuclear heterometallic compounds has aroused significant attention [1–3] not only because of their unique molecular configurations, but also due to distinctive properties and versatile applications in nano-technology [4,5], materials science [6,7] and magnetism [8–11]. What's more, the synthesis of polynuclear heterometallic compounds has not merely greatly enriched the advantages of lanthanide ions, more importantly combined excellent properties of both lanthanide and transition metals. Although quite a few of polynuclear lanthanide heterometallic compounds featuring fantastic structures have been reported (e.g., spherical [12–14], ladder [15–17], tubular [18,19], helical [20–22] clusters), it still exists a significant challenge in synthesis of nanosized heterometallic clusters.

Currently, there are two mainstream methods to synthesize the nanosized polynuclear heterometallic compounds with rare-earth and transition metals via suitable ligands [23]. The first approach is the two-step synthesis. The transition metal first coordinates with the ligand to form a preformed complex, then the foregoing preformed complex reacts with the rare earth ions. By this way, we can obtain the objective product [24,25]. The second is the one-pot synthesis with the incorporation of the starting metallic oxide and judicious ligands to form the polynuclear or high-nuclearity complexes. Although some difficulties exist in the second approach, for example, intricate assembly processes, unpredictable results, it still arouses the enthusiasm of the researchers. In this paper, we use the latter approach to synthesis target products and it has enjoyed tremendous success [26–28]. As described above, from the latter approach we can see that the choice of ligands [29–31] plays an indispensable role during the synthesis of nanosized heterometallic compounds. Moreover, the organic ligands may decompose into small molecular anionic species in the assembly processes. These species could act as counterions or auxiliary ligands to induce the formation of the clusters, which is also of crucial importance. Taking the above into consideration, the flexible ligand iminodiacetic acid (IDA) is strictly satisfied the aforementioned demands, which possesses two coordinate carboxylates, one nitrogen atom and can also decompose carbonate, glycine and oxalate as the auxiliary ligand.

In this context, we have successfully synthesized two Ni-Ln nanosized polynuclear clusters under the connection of iminodiacetic acid, formulated as $[Nd_{20}Ni_{21}(IDA)_{21}(NH_2CH_2COO)_6(OAc)_3(CO_3)_6(C_2O_4)_3(\mu_3\text{-}O)_9(\mu_3\text{-}OH)_{12}(\mu_2\text{-}OH)_3\cdot 12H_2O]\cdot 32H_2O$ (**1**), and $[Na_3Pr_{20}Ni_{21}(IDA)_{21}(NH_2CH_2COO)_6(OAc)_9(CO_3)_6(C_2O_4)_3(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_{15}(\mu_2\text{-}OH)_3\cdot 12H_2O]\cdot 15H_2O$ (**2**) (See the experiment section of the supporting information). Single crystal X-ray structural analysis shows that the structure of compound **1** and **2** are analogous. They are comprised of two $[Ln_{10}Ni_{12}]$ (Ln=Nd(**1**), Pr(**2**)) units by sharing three Ni4 ions on the one plane. It is worth mentioning that compared with wide research on classical mononuclear or lower-nuclearity lanthanide clusters, polynuclear or high-nuclearity (over 40 metal ions) analogues are relatively rare [32–36]. The magnetic properties of them reveal antiferromagnetic change interaction in clusters.

Compound **1** crystallizes in the hexagonal crystal system, space group $P\overline{6}c2$. As shown in Fig. 1, umbrella-like asymmetric unit $[Nd_{10}Ni_{12}]$ in compound **1** is formed by twelve IDA ligands, three

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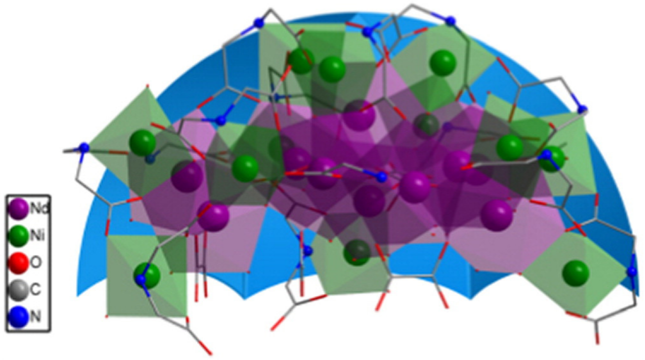

Fig. 1. View of the asymmetric unit of compound **1**.

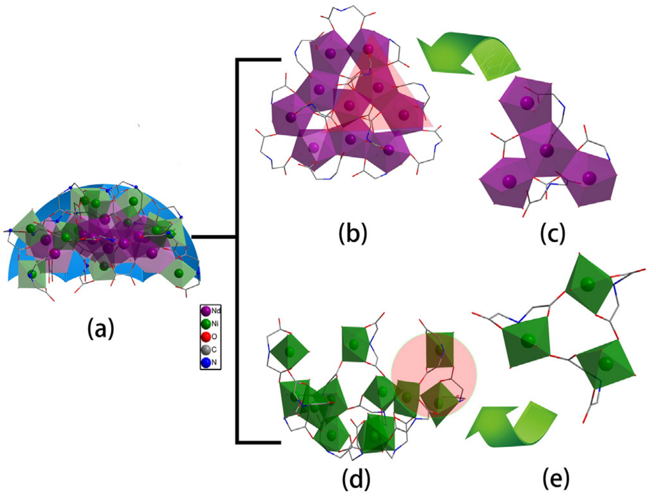

Fig. 2. (a) The $[Nd_{10}Ni_{12}]$ unit in compound **1**; (b) The $[Nd_{10}]$ unit; (c) The $[Nd_4]$ cluster; (d)The $[Ni_{12}]$ unit; (e) The $[Ni_3]$ core.

$NH_2CH_2COO^-$, two CH_3COO^- ions as well as CO_3^{2-}, $C_2O_4^{2-}$, μ_3-OH, μ_3-O, μ_2-OH groups. In addition, it also involves eleven coordination water molecules as well as five lattice water molecules.

All Nd(III) ions in compound **1** are all nine-coordinated and adopt a tricapped trigonal prism coordination configuration. As depicted in Fig. S1, four types of coordination modes are involved in the inner Nd_{20} core: (i) Nd2 is connected with two carboxylate oxygen (O_{coo}) atoms (O28, O45) from two different IDA ligands, four oxygen atoms (O3, O8, O12, O1) from auxiliary ligands carbonate and glycine, one oxygen atom (O49) from CH_3COO^- and other two bridging oxygen atoms (O5, O22); (ii) Compared with Nd2, Nd5 is linked by three O_{coo} atoms (O26, O33, O41) from IDA ligands, one oxygen atom (O16) from oxalate, one oxygen atom (O12) from carbonate as well as five bridging oxygen atoms (O9, O16, O19, O22, O47); (iii) Nd6 is bridged by six oxygen atoms (O1, O8, O16, O37, O40, O51) and one nitrogen atom (N8) from IDA as well as other auxiliary ligands which are decomposed by IDA, the rest two oxygen atoms (O9, O11W) from μ_3-OH group and water molecular respectively; (iv) Nd7 is nine-coordinated by six oxygen atoms (three O13, three O3) from IDA ligands and carbonate ions, three oxygen atoms (two O5, O28) from bridging oxygen groups μ_3-OH and μ_3-O^{2-}. Additionally, all Ni(II) ions in **1** are six-coordinated, exhibiting octahedral coordination geometry. Similar as Nd(III) ions, Ni(II) ions also employ four different coordination modes (Fig. S2).

As depicted in Fig. 2a, the $[Nd_{10}Ni_{12}]$ unit in **1** contains ten Nd(III) ions, which are encapsulated by twelve Ni(II) ions and yield an umbrella-shaped cluster. On the one hand, four Nd(III) ions linked by two IDA ligands, one glycine ligand as well as two carbonate ions, thus forming a triangular $[Nd_4]$ cluster (Fig. 2c). Meanwhile, three $[Nd_4]$ clusters tightly couple together by sharing Nd7 atom to form $[Nd_{10}]$ unit (Fig. 2b), in which IDA ligands are in mode II and III (Fig. S3a), glycine ligand (Fig. S3b) and carbonate ions are in mode I (Fig. S4). On the other hand, three Ni atoms linked together to form a $[Ni_3]$ core (Fig. 2e) and then four $[Ni_3]$ clusters are further connected by IDA ligands to form the outer $[Ni_{12}]$ unit (Fig. 2d). Inspired by the above mentioned, according to the different coordination environment of carboxylate groups, IDA, glycine and carbonate ligands could be divided into diverse modes (Fig. S3 and S4), which are crucial in the construction of two main building blocks of $[Nd_{10}]$ and $[Ni_{12}]$. Finally, the inner $[Nd_{10}]$ unit and the outer $[Ni_{12}]$ unit form $[Nd_{10}Ni_{12}]$ unit via the IDA ligands (Fig. 2a). As for the structure, the configuration of the two compounds is not without precedent reported in the literature, previous research on high-nuclearity heterometallic cluster had yield the analogous $Ln_{20}Ni_{21}$ (Ln=Nd and Pr) cluster [29]. What is worth mentioning is that the extraframework species and synthetic methods are different. Compared with the previous work, carbonate substitute the nitrate, which acts as the anion template, resulting from the oxide is replaced by nitrate. Additionally, the decomposition products of IDA are not the same. What's more, the solvent, temperature and reaction time are also distinctive. As a consequence, these two compounds of the article are worth studying and researching.

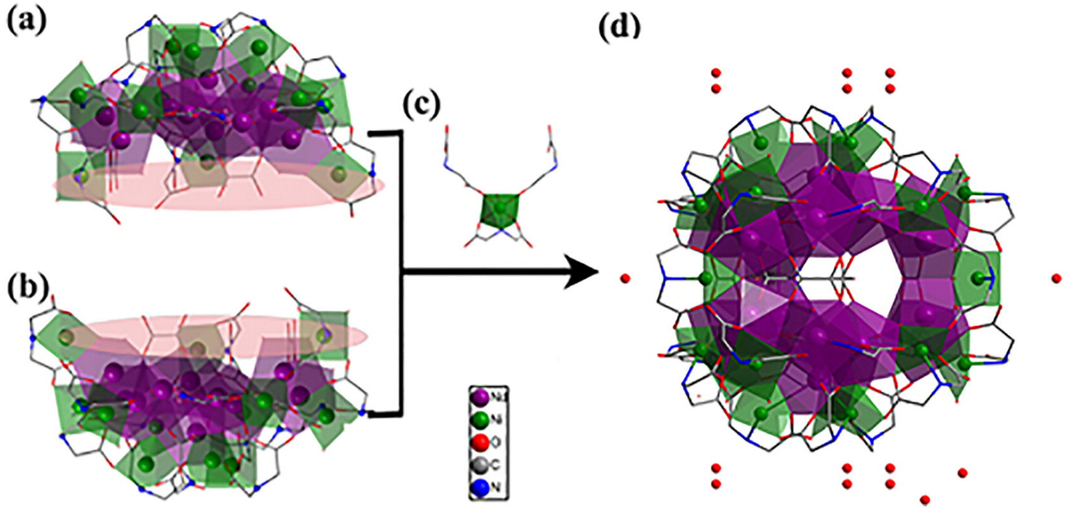

Fig. 3. (a) The top $[Nd_{10}Ni_{12}]$ unit in compound **1**; (b) The bottom $[Nd_{10}Ni_{12}]$ unit in compound **1**; (c) The coordination environment of Ni4 ion in compound **1**; (d) The structure of compound **1** (H atoms were omitted for clarity).