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The first lanthanide-templated molecular wheel containing six copper ions†

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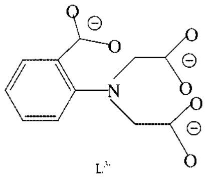
A novel copper(II)–praseodymium(III) hetero-polynuclear complex $[Cu_6PrL_6][Pr(H_2O)_{10}]\cdot 14H_2O$ (H_3L: *N*-carboxymethyl-*N*-(2-carboxyphenyl) glycine acid) has been structurally and magnetically characterized, which consists of a molecular wheel of six Cu(II) ions with a Pr(III) ion axle.

High-nuclearity metal complexes are of special current interest due to their potential magnetic, optical, electronic and catalytic properties.[1] The design and synthesis of the large cluster is one of the most challenging fields, especially for the relatively unexplored 4f–3d heteronuclear clusters owing to the distinct difference in the chemical nature of transition and lanthanide elements.[2] Amino-carboxylate ligands are good candidates for constructing 4f–3d molecular materials. Some interesting structures were previously documented based on this kind of ligand.[3] Very recently, we have succeeded in preparing a heptanuclear cluster $[LnCu_6(\mu_3\text{-}OH)_3(Hima)_2(ima)_4][ClO_4]_2\cdot 25H_2O$ (H_2ima = iminodiacetic acid).[4] Subsequently, an aminotricarboxylate ligand L^{3-} (Chart 1) has been used to assemble 4f–3d heteronuclear compounds. Unexpectedly, a wheel-shaped heptanuclear cluster $[Cu_6PrL_6][Pr(H_2O)_{10}]\cdot 14H_2O$ **1**, was obtained. Herein, its structure and magnetic properties are reported.



L^{3-}

Chart 1

Compound **1** was prepared by the reaction of praseodymium hydroxide, copper(II) perchlorate and NaH_2L in a 1 : 3 : 3 molar ratio in aqueous solution. Blue–green prismatic crystals were obtained after two weeks.‡

X-Ray diffraction analysis revealed that compound **1** consists of one coordination anion $[Cu_6PrL_6]^{3-}$, one cation $[Pr(H_2O)_{10}]^{3+}$, and some disordered crystal lattice water molecules.§ An interesting feature of the structure lies in the $[Cu_6PrL_6]^{3-}$ anion moiety, in which the Pr(III) ion is encapsulated by a macrocycle composed of six Cu(II) ions as depicted in Fig. 1. The Pr^{3+} ion is located on a C_3 axis and is twelve coordinated by six chelating carboxyl groups from six different ligands, forming an icosahedron. Each ligand employs the carboxyl group of the benzene ring to connect Cu and Pr in a rare tridentate 1,1,3-bridging mode, similar to that observed in $Ln_2M_3(edta)_3(H_2O)_{11}\cdot 12H_2O$[3] and $[Gd_2Mn_2O_2(O_2CCMe_3)_8(HO_2CCMe_3)_2(MeOH)]$.[5] One of the two amino-carboxyl groups coordinates to the Cu ion in a monodentate fashion, whereas another one bridges the two neighboring Cu ions, producing a wheel containing six Cu ions. Strictly speaking the six Cu(II) ions are not in a perfect plane but arranged in such a way that three Cu1 and Cu2 sets yield a double layer with Pr(III) embedded in the middle. However, the inter-layer distance (0.92 Å) is not large enough to form a trigonal antiprismatic cage containing the Pr(III) ion like in $[LnCu_6(\mu_3\text{-}OH)_3(Hima)_2(ima)_4][ClO_4]_2\cdot 25H_2O$.[4] On the contrary, the Pr(III) ion protrudes out of the double layer (the radius of Pr(III) is larger than 0.92 Å), much like a wheel hub. We believe that the template effect of Pr should have a key contribution to the formation of the wheel-like cluster core. The radius of the wheel, namely the Pr ··· Cu distance is 4.6225 Å and the neighboring Cu1 ··· Cu2 average separation in the ring is 4.6916 Å.

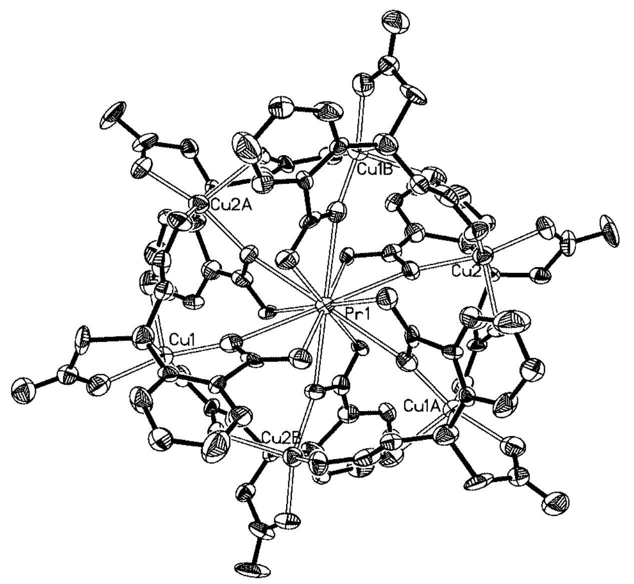


Fig. 1 An ORTEP[13] view of the wheel-like cluster core of **1**. The $Pr(H_2O)_{10}^{3+}$ cation, lattice water molecules and all hydrogen atoms are omitted for clarity.

The centered wheel structure is rather common in heptanuclear transition metal clusters, such as Cu_6Na, Co_6Na, Fe_6Na,[7] where the Na^+ ion occupies the central position as a cation template, and also Zn_7, Mn_7, Cu_7, which are homometallic.[8] They represent an important class of structural motif. However, this structural motif is significantly absent in 4f–3d heteronuclear clusters. Up to now, the three known LnM_6 heptanuclear

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† Electronic supplementary information (ESI) available: χ_m^{-1} and χ_mT *versus* T plots for **1** and part of the structure of the cluster core of **1**. See http://www.rsc.org/suppdata/dt/b0/b003670f/

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clusters were: $[Sm\{Ni(pro)_2\}_6][ClO_4]_3\cdot6MeOH$ (pro = proline) in which the Sm(III) ion is located in the center of a perfect octahedron formed by six Ni(II) ions;[9] $[\{Ni(L')\}_6La](ClO_4)_3$ (L′ = 1,9-dicarboxyl-2,8-dimethyl-dienamin(3,7)), has the same structural motif as $SmNi_6$;[6] and $[LnCu_6(\mu_3\text{-}OH)_3(Hima)_2(ima)_4][ClO_4]_2\cdot25H_2O$, in which the Ln(III) ion is embedded at the center of the trigonal prism yielded by six Cu(II) ions.[4] Compound **1** is significantly different from those mentioned above and also dissimilar to the metallacrown lanthanide complex $Ln(NO_3)_3[15\text{-}MC_{Cu(II)N(picha)}\text{-}5]$ (picha = picoline hydroxamic acid) in which all the metal ions are almost coplanar.[10] The wheel-like structure motif with a lanthanide ion as the central axle is very unique in 4f–3d clusters and serves as the first lanthanide-centered molecular wheel containing six d-block ions.

The Pr(III) ion in the cation $[Pr(H_2O)_{10}]^{3+}$ is coordinated by ten water molecules, some of which are disordered. It plays an important role in charge compensation for the cluster core. Some water molecules are present in the crystal lattice, which con-solidify the cluster structure through hydrogen bonding.

The temperature dependence of the magnetic susceptibility in the temperature range 4–300 K under 5 kOe applied field was studied for compound **1**. The $\chi_m T$ value at room temperature is 4.90 $cm^3\ mol^{-1}$ K, slightly smaller than 5.25 $cm^3\ mol^{-1}$ K for the two free Pr^{3+} and six spin-only Cu^{2+} ions. $\chi_m T$ remains almost constant from 300 to 100 K, then decreases dramatically as the temperature is lowered below 50 K. The data fit well with the Curie–Weiss law, giving $C = 5.09\ cm^3\ mol^{-1}$ K, and $\theta = -6.6$ K. The magnetization value at 50 kOe applied field at 5 K is 3.65 $\mu_B\ mol^{-1}$, far lower than the saturation value 12.4 $\mu_B\ mol^{-1}$ for the non-interacting free ions based on the Brillouin function. These results suggest that (a) there is no detected magnetic coupling between metal ions at high temperature ($T > 100$ K); (b) reduction of $\chi_m T$ and a small magnetization value at low temperature should arise from antiferromagnetic coupling of the six Cu^{2+} ions within the ring, and the crystal field splitting of Pr^{3+} ions (one at the center of the wheel and the other isolated), which all trend a non-magnetic singlet; (c) the nature of the interactions between Pr^{3+} and Cu^{2+} cannot be extracted due to the complication of the system,[10] and may be negligibly small compared with the Cu–Cu coupling, as in metallacrown-5(15-MC-5).[11]

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Notes and references

‡ The sodium derivative of the ligand *N*-carboxymethyl-*N*-(2-carboxyphenyl)glycine, (NaH_2L) was synthesized according to a modified literature method.[12] *o*-Aminobenzoic acid, chloroacetic acid and sodium carbonate were mixed in a 1 : 2 : 2 molar ratio in aqueous solution. The mixture was stirred and refluxed for 3 h, then the solution was acidified to pH = 1 using hydrochloric acid. The resulting white precipitate was collected and re-crystallized with ethanol. Compound **1** was prepared by mixing praseodymium hydroxide (0.13 mmol), copper(II) perchlorate (0.38 mmol) and NaH_2L (0.38 mmol) in aqueous solution (15 mL) under stirring and heating. The mixture gradually formed a clear blue solution, then was condensed to *ca.* 10 mL. The resulting solution was filtered and the filtrate was allowed to stand at room temperature. On slow evaporation, blue–green prismatic crystals were isolated after two weeks. Elemental analysis: Calc. for $C_{66}H_{96}Cu_6N_6O_{60}Pr_2$: C, 30.5; H, 3.70; N, 3.23. Found: C, 29.8; H, 3.88; N, 3.12%. Using a similar procedure the lanthanum analog was also obtained as microcrystals. The ratio of La : Cu is 1 : 6 checked by ICP, and Calc. for $C_{66}H_{96}Cu_6N_6O_{60}La_2$: C, 30.5; H, 3.70; N, 3.24. Found: C, 29.1; H, 3.77; N, 3.10%.

§ Crystal data for **1**: $C_{66}H_{96}Cu_6N_6O_{60}Pr_2$, $M = 2596.55$, rhombohedral, space group $R3c$, $a = b = c = 18.186(2)$ Å, $\alpha = \beta = \gamma = 69.784(17)°$, $U = 5119.1(10)$ Å^3, $Z = 2$, $T = 294$ K, μ(Mo-Kα) = 2.257 mm^{-1}, $R1$ and $wR2$ are 0.0615 and 0.1575, respectively for 457 parameters and 4131 reflections [$I > 2\sigma(I)$]. CCDC reference number 186/2019. See http://www.rsc.org/suppdata/dt/b0/b003670f/ for crystallographic files in .cif format.

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