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A Remarkable Member of the Polyoxometalates: The Eight-Nickel-Capped α-Keggin Polyoxoazonickelate

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The eight-nickel-capped polyoxoazonickelate, $[Ni_{20}(OH)_{24}(MMT)_{12}(SO_4)](NO_3)_2 \cdot 6H_2O$ (**1**; MMT = 2-mercapto-5-methyl-1,3,4-thiadiazole), has been synthesized, which has an α-Keggin structure with eight nickel caps. In this structure, the polyatom is the late transition metal Ni^{II}; the central heteroatom is S, and the organic terminal ligand becomes the primary part of the Keggin structure. This is a Keplerate-type cluster, which shows a central Ni^{II}_{12} cuboctahedron formed by the 12 Ni^{II} centers of the classical α-Keggin core and a Ni^{II}_8 hexahedron formed by the eight nickel caps.

Polyoxometalates (POMs) are a very interesting and useful class of inorganic compounds.[1–4] This has been known for about 200 years since Berzelius[5] reported the first POM, $(NH_4)_3PMo_{12}O_{40} \cdot nH_2O$. Because of their unique structures, POMs possess excellent molecular properties and have various applications in different areas such as catalysis, magnetism, materials science, and medicine.[6–8] The Keggin structure,[9] with a general formula $[XM_{12}O_{40}]^{3-}$ (where X = Si, As, P, Fe, etc., and M = Mo, W, V, Nb, etc.), is one of the most representative structures of POMs. It consists of four M_3O_{13} triad units formed by edge-sharing octahedra, connecting each other by vertices, and a tetrahedral heteroatom encapsulated within the center. Recently, some novel Keggin-type POMs have been reported. Nyman et al.[10] reported the first heteropolyniobate, $K_{12}[Ti_2O_2][SiNb_{12}O_{40}] \cdot 16H_2O$, which contained chains of silicododecaniobate Keggin ions. Winpenny et al.[11] reported some reverse-Keggin ions, such as $[Mn(PhSb)_{12}O_{28}\{Mn(H_2O)_3\}_2\{Mn(H_2O)_2(AcOH)\}_2]$. Through investigation of the previous research, we find that, in the existing structures of traditional POMs, the polyatoms are almost always early transition metals but are rarely available for the late transition metals. A few years ago, Lippard et al.[12] reported the first late-transition-metal Fe^{III} Keggin ion with an open-shell electronic structure, $[Fe_{13}O_4F_{24}(OMe)_{12}]^{5-}$, which may be the closest example. The late transition metals, such as Fe, Co, and Ni, are very important functional elements with wonderful properties. We consider that POMs with late transition metals as the polyatoms may extend not only their structural features but also their properties. Moreover, late transition metals can be easily linked by organic ligands to form metal–organic

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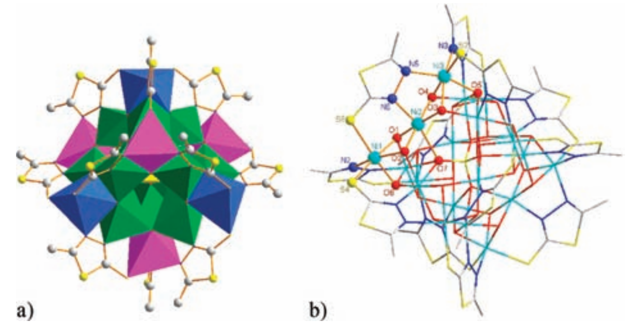

Figure 1. (a) Polyhedral and ball-stick structure representation of **2**. The green octahedra represent NiO_5N units; the yellow tetrahedron in the center represents the $\{SO_4\}$ core; the blue octahedra represent the NiO_3S_2N caps; the pink octahedra represent the NiO_3N_2S caps. (b) Representation of the coordinated environment of Ni^{II} in **2**. Color code: Ni, cyan; N, blue; O, red; S, yellow; C, gray. H atoms have been omitted for clarity.

frameworks (MOFs). Accordingly, we attempt to synthesize new POMs using late transition metals as the polyatoms, through the approach of constructing MOFs.

Herein, we report an eight-nickel-capped α-Keggin polyoxoazonickelate, as shown in Figure 1a, the polyatom of which is the late transition metal Ni^{II} and the central heteroatom of which is S. This is a Keplerate-type[13] cluster with high symmetry. The solvothermal reaction between 2-mercapto-5-methyl-1,3,4-thiadiazole (MMT; Figure S1 in the Supporting Information) and nickel nitrate, in a mixed solvent of water and ethanol, in the presence of triethylamine and ethanolamine resulted in green octahedral crystals of $[Ni_{20}(OH)_{24}(MMT)_{12}(SO_4)](NO_3)_2 \cdot 6H_2O$ (**1**).[14] Single-crystal X-ray diffraction (XRD)[15] analysis shows that compound **1** is tetragonal and crystallizes in the space group *I*4. The cation complex $[Ni_{20}(OH)_{24}(MMT)_{12}(SO_4)]^{2+}$ (**2**), which has a noncrystallographic T_d symmetry, is the first example of an icosanuclear nickel cluster consisting of the open-shell α-Keggin ion $[Ni_{12}(OH)_{24}(MMT)_{12}(SO_4)]^{14-}$ (**3**), capped by eight Ni^{II} atoms. We name this compound polyoxoazonickelate, and it is a remarkable member of the POMs. Figure 1b is a representation of the coordinated environment of Ni^{II} in this structure.

In the structure of **2**, the 20 Ni^{II} centers are all six-coordinated and in distorted octahedral coordination. From Figure 1b, we can find that there are three independent Ni^{II} centers showing three different coordination environments. The $Ni1^{II}$ center is coordinated to three μ_3-O atoms, two S atoms, and one N atom, just like the blue octahedral caps represented in Figure 1a, and there are four such Ni^{II} centers. The $Ni2^{II}$ center is coordinated to four μ_3-O atoms, one μ_4-O atoms from the $\{SO_4\}$ core, and one N atom, just like the green octahedra represented in Figure 1a. The α-Keggin ion of **3** is consists of 12 such Ni^{II} atoms. The $Ni3^{II}$ center is coordinated to three μ_3-O atoms, two N atoms, and one S atom, just like the pink octahedral caps represented in Figure 1a, and there are four such Ni^{II} centers.

From Figure 1a, we can easily find the part of the classical α-Keggin structure **3** after taking out the eight nickel caps. The central tetrahedral $\{SO_4\}$ core with a S−O distance of 1.507(8) Å is surrounded by 12 octahedrally coordinated Ni^{II} atoms, which are bridged by 24 protonated O atoms. The Ni−O distances are in the range of 1.949(11)−2.092(12) Å. One of the most remarkable features of this structure is that each of the 12 Ni^{II} atoms in **3** is coordinated to a terminal organic ligand MMT with an average Ni−N distance of 2.076(13) Å, which is different from the traditional POMs. There are a total of 12 N atoms from different organic MMT ligands. The organic terminal ligand becomes the primary part of this α-Keggin structure. Three edge-sharing octahedral NiO_5N units form a triad metal unit, and four such units connect to each other by vertices, forming the cage of the α-Keggin structure.

Theoretically, this isolated α-Keggin ion is unstable because of its extremely high negative charge. It should be lowered to remain stable. The following two facts play important roles in stabilizing this α-Keggin ion. First, the protonation:[16] although the bridging O atoms have high electron densities, when they are protonated, the electron densities can be reduced so that the whole negative charge can be lowered. Second, the cationic caps:[17] the eight octahedral Ni^{II} caps can also lower the whole charge effectively. As a result, this α-Keggin ion is stabilized by protonations of the 24 bridging O atoms and capping with eight Ni^{II} cations, leading to the stable structure of **2**. Through investigation of the thermogravimetric analysis (TGA) of this compound (Figure S2 in the Supporting Information), we found that, below 278 °C, it only released the free H_2O molecules, which indicated that the structure was stable below 278 °C. The XPRD spectrum (Figure S3 in the Supporting Information) can also prove that the framework of **2** was stable and remained unchanged below 278 °C.

The positions of the eight octahedral nickel caps are also shown in Figure 1a. For every triad metal unit, there is one octahedral nickel cap, the blue octahedral NiO_3S_2N, which is edge-sharing with the triad metal unit. The S and N atoms are

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(14) Synthesis of $[Ni_{20}(OH)_{24}(MMT)_{12}(SO_4)](NO_3)_2 \cdot 6H_2O$ (**1**): A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (0.290 g, 1 mmol), MMT (0.132 g, 1 mmol), triethylamine (0.102 g, 1.67 mmol), ethanolamine (0.072 g, 0.717 mmol), 4 mL of H_2O, and 4 mL of C_2H_5OH was sealed in a 23 mL Teflon-lined stainless steel vessel and heated to 110 °C for 3 days and then cooled to room temperature at a rate of 0.1 °C/min. Green octahedral crystals were obtained. The product was washed with C_2H_5OH and dried in air (39% yield based on Ni^{II}). Elem anal. Calcd for $C_{36}H_{72}N_{26}Ni_{20}O_{40}S$: C, 12.40; H, 2.07; N, 10.45; S, 23.87. Found: C, 12.36; H, 2.12; N, 10.50; S, 23.86.

(15) Crystal data of **1**: $C_{36}H_{72}N_{26}Ni_{20}O_{40}S_{26}$, $M_r = 3484.88$, tetragonal, space group *I*4, $a = 13.7540(19)$ Å, $b = 13.7540(19)$ Å, $c = 28.029(6)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 5302.3(15)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.183$ g/cm^3, $R_{int} = 0.0621$, final R1 = 0.0552 (wR2 = 0.1318) for 2966 independent reflections [$I > 2\sigma(I)$]. Data were collected on a Bruker Smart-Apex CCD diffractometer with Mo Kα ($\lambda = 0.71073$ Å) at 298 K using the ω-scan technique. Multiscan absorption corrections were applied. The structure was solved by direct methods and refined by full matrix least squares on F^2 using *SHELXTL-97* software. The Flack parameter of 0.00(2) for **1** indicates that the absolute configuration is correct.

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from the different MMT ligands. The Ni−O distances are 2.023(10), 2.060(11), and 2.109(10) Å, respectively; the Ni−S distances are 2.407(6) and 2.544(5) Å; the Ni−N distance is 2.208(12) Å. There are four caps of this kind. In the position where the three triad metal units connect to each other, there is another kind of octahedral nickel cap, the pink octahedral NiO_3N_2S, which is vertex-sharing with the triad metal units. The S and N atoms are also from the different MMT ligands. The Ni−O distances are 1.994(11), 2.084(11), and 2.092(12) Å, respectively; the Ni−N distances are 2.155(10) and 2.217(11) Å; the Ni−S distance is 2.390(5) Å. There are also four caps of this kind.

We can understand this overall structure further more from the geometrical perspective. This is a highly symmetrical structure of the Keplerate type.[18] About 10 years ago, Müller and his colleagues used the term of Keplerate for the first time to describe structures containing Platonic and Archimedean solids one inside another.[19] The Archimedean solid is a kind of highly symmetric polyhedron in geometry, consisting of two or more types of regular polygons sharing the same vertices; the Platonic solid is a polyhedron with a regular polygon; that is to say, it is a regular polyhedron. In the structure of **2**, the 12 six-coordinated Ni^{II} centers of the classical α-Keggin core form an cuboctahedron, which is an Archimedean solid with eight triangular faces and six square faces. The eight Ni^{II} caps form a unique Platonic solid, Ni^{II}_8 hexahedron, i.e., a cube. Accordingly, this structure shows a central Ni^{II}_{12} cuboctahedron and a Ni^{II}_8 hexahedron, which can be called a Keplerate, just like that shown in Figure 2a. It is also very interesting when we pay attention to the 24 bridging O atoms again. These protonated O atoms form a rhombicuboctahedron Archimedean solid with 8 triangular faces and 18 square faces, as shown in Figure 2b. So, this structure can also be seen as a Keplerate having two Archimedean solids, cuboctahedron and rhombicuboctahedron, which are formed by the 12 Ni^{II} centers of the classical α-Keggin core and the 24 protonated bridging O atoms, respectively, inside the unique Platonic solid Ni^{II}_8 hexahedron formed by the eight nickel caps. This new structure shows extraordinary aesthetic beauty with high symmetry.

We also explore the magnetic and luminescence properties of this compound. The magnetic susceptibility studies indicate that there are strong antiferromagnetic exchange interactions between the Ni^{II} atoms in **1** (Figure S4 in the Supporting Information). The luminescence emission spectrum of **1** is the same as that of the MMT ligand except for the intensity (Figure S5 in the Supporting Information).

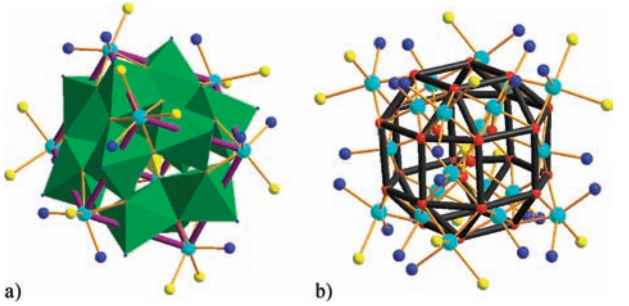

Figure 2. (a) Representation of the Keplerate-type structure of **2** with the cuboctahedron Archimedean solid formed by the 12 Ni^{II} centers of the α-Keggin core inside the Ni^{II}_8 hexahedron Platonic solid (violet polyhedron) formed by the nickel caps. (b) Representation of the rhombicuboctahedron Archimedean solid formed by the 24 bridging O atoms (black polyhedron). Color code: Ni, cyan; N, blue; O, red; S, yellow. The terminal ligands and the H atoms have been omitted for clarity.

In summary, we report a remarkable member of the POMs named polyoxoazonickelate, $[Ni_{20}(OH)_{24}(MMT)_{12}(SO_4)](NO_3)_2\cdot 6H_2O$ (**1**), which has an α-Keggin structure with eight nickel caps. In this structure, the polyatom is the late transition metal Ni^{II}, the central heteroatom is S, and the organic terminal ligand becomes the primary part of the Keggin structure. It can be seen as a Keplerate with high symmetry. Our idea, which is the synthesis of POMs using the late transition metals through construction of MOFs, is distinctive and different from the traditional synthesis idea of POMs and thus may provide access to a wide range of POMs with extraordinary structures and potential properties or functionalities. We consider that it may greatly advance the development of the POM chemistry of late transition metals. In our further studies, we will try our best to synthesize more such novel POMs with excellent structures, investigate the driving forces and the underlying principles that govern their assembly processes, and explore their properties or potential applications.

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Supporting Information Available: X-ray crystallographic data in CIF format and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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