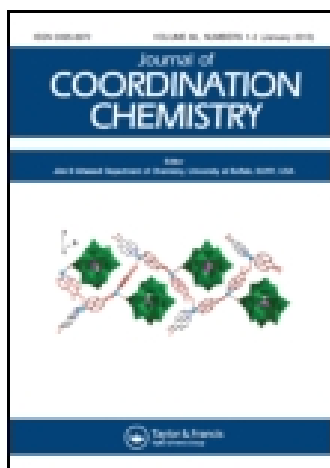


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Dodecanuclear water cluster in bowl: microwave-assisted synthesis of a heptanuclear cobalt(II) cluster

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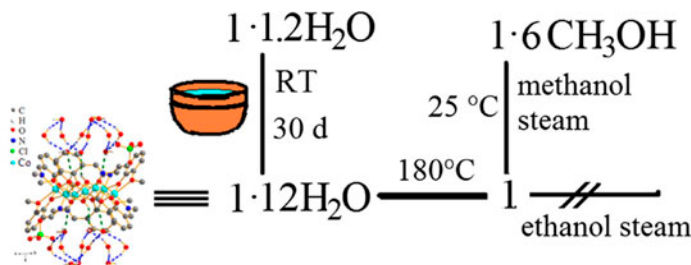
Dodecanuclear water cluster in bowl: microwave-assisted synthesis of a heptanuclear cobalt(II) cluster

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Using microwave assisted heating solvothermal method, a double-bowl-like heptanuclear cluster $[\text{Co}_7(\text{mmp})_6(\text{OH})_6]_2(\text{ClO}_4)_2 \cdot 12\text{H}_2\text{O}$ (**1**·12H₂O) has been synthesized. We study the thermolysis of **1**·12H₂O through TG and XRD. **1** was formed through heating **1**·12H₂O. Magnetic behavior between **1** and **1**·12H₂O indicates hydrogen bonds playing an important role for transferring magnetic exchange effects. **1** shows a single molecular magnet behavior under 2 K.

A heptanuclear double-bowl-like cluster $[\text{Co}_7(\text{mmp})_6(\text{OH})_6]_2(\text{ClO}_4)_2 \cdot 12\text{H}_2\text{O}$ (**1**·12H₂O, Hmmp is 2-methoxy-6-methyliminomethyl-phenol) has been synthesized through the microwave-assisted reaction of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with 2-hydroxy-3-methoxy-benzaldehyde (Hhmb) and methylamine in mixed solvent (acetonitrile : distilled water = 9 : 1) for 29 min. **1**·12H₂O was heated until 180 °C and it formed a non-water complex $[\text{Co}_7(\text{mmp})_6(\text{OH})_6]_2(\text{ClO}_4)_2$ (**1**). The core of **1**·12H₂O can be described as a double bowl, while the dodecanuclear water cluster stands on the bowl. Magnetic investigations show that **1**·12H₂O and **1** display ferromagnetic interaction between cobalt ions. Moreover, **1** shows single molecular magnet behavior under 2 K. Magnetic studies indicate that hydrogen bond plays a vital role in transferring magnetic exchange effects.

Keywords: Heptanuclear cluster; Dodecanuclear water cluster; Hydrogen bonds; Magnetic exchange

1. Introduction

Attention has been given to the design and synthesis of the paramagnetic polymetallic clusters since the discovery of “single-molecule magnets” (SMMs) [1]. The search for ligands

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to suit their respective needs is one of the most important processes to advance this research. Schiff bases are widely used in the synthesis of magnetic clusters [2]. An effective and facile approach for the synthesis of such clusters is still the appropriate choice of well-designed organic ligands as bridges or terminal groups with metal ions or metal clusters as nodes. Previous investigations implied that the Hhmb derivatives as ligands constructed the metal clusters favoring ferromagnetic coupling through μ_3 -O-bridges [2(e), 3] and towards SMM behavior [2(e)]. Herein, we chose the analogous 2-methoxy-6-methyliminomethylphenol to serve as a chelating/bridging ligand to bring metal ions into a new heptanuclear double-bowl-like cluster $[\text{Co}_7(\text{mmp})_6(\text{OH})_6]_2 \cdot (\text{ClO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Microwave heating has been introduced into solvothermal synthesis, as a new method for synthesizing the polymetallic clusters, resulting in higher yields, shorter reaction times, and also in the formation of completely new products [3(b) and (c), 4, 5].

Compounds containing dimer water [6, 7], water rings [6–11], water chains [12–14], metal–water chains [15], water network [16(a) and (b)], water ring chains [16(c)], and water–methanol clusters [17] have considerable interest because they are the potentially important water forms. Water chains appear to facilitate the selective permeation [18] of water across the membranes and are also important in the control of proton fluxes in a variety of biomolecules. Tetramer, pentamer [19], hexamer [20], heptamer [21], octamer [22], nonamer [23], decamer [24], and dodecamer [25] water clusters have been isolated from different crystalline hosts. Herein, using microwave-assisted synthesis and cobalt(II) ions and a new Schiff base Hmmp as the reactants, a dodecamer water cluster has been observed in the double-bowl-like heptanuclear cobalt cluster $[\text{Co}_7(\text{mmp})_6(\text{OH})_6]_2 \cdot (\text{ClO}_4)_2 \cdot 12\text{H}_2\text{O}$.

2. Experimental

2.1. Materials and physical measurements

All chemicals were commercially available and were used as received. Microwave synthesis is carried out using a XH-800C microwave digestion system. Elemental analyses (CHN) were performed using an Elementar Vario-EL CHNS elemental analyzer. FT-IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Bio-Rad FTS-7 spectrophotometer. TG analyses were performed on a TG209. Powder X-ray diffraction (PXRD) was measured with a Rigaku D/max 2500v/pc diffractometer. The crystal structure was determined by single-crystal X-ray diffraction, using SHELXL crystallographic software for molecular structure. Magnetization measurements were carried out with a Quantum Design MPMS-XL7 SQUID to 5 T for both $\mathbf{1} \cdot 12\text{H}_2\text{O}$ and $\mathbf{1}$.

2.2. Synthesis

A mixture of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.360 g, 1 mM), Hhmb (0.152 g, 1 mM), methylamine (0.5 mL (50%)), acetonitrile (27 mL), and water (3 mL), with pH adjusted to 7.5 by the addition of triethylamine, was poured into a 60-mL Teflon-lined autoclave and then inserted into the cavity of a microwave reactor. The reaction mixture was maintained at $T = 140\text{ }^\circ\text{C}$, power = 300 W, and pressure = 79.4 psi for a total of 29 min. After cooling (ca. 120 min), red crystals of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ were collected by filtration, washed with water, and then dried in air. The pure-phase crystals of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ were obtained by manual separation (Yield: 135 mg, ca. 49.35% based on Co). Anal. Calcd for $\mathbf{1} \cdot 12\text{H}_2\text{O}$ (%): $\text{C}_{54}\text{H}_{90}\text{Cl}_2\text{N}_6\text{Co}_7\text{O}_{38}$: C,

33.87; H, 4.74; N, 4.39. Found (%): C, 33.85; H, 4.77; N, 4.36. IR data for $1 \cdot 12\text{H}_2\text{O}$ (KBr, cm^{-1} , figure S1, see online supplemental material at <http://dx.doi.org/10.1080/00958972.2014.964221>): 3443(s), 2929(m), 1633(s), 1472(m), 1376(w), 2220(m), 1099(s), 746(w), 621(w), 483(w).

2.3. X-ray crystallography

The diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173 K and using the $\omega - \theta$ scan mode ($2.41^\circ \leq \theta \leq 25.19^\circ$). Raw frame data were integrated with the SAINT program [26]. The structure was solved by direct methods using the SHELXS-97 and was refined by the full-matrix-least-squares on F^2 [26]. An empirical absorption correction was applied with SADABS [26]. All non-hydrogen atoms were refined anisotropically. Hydrogens of water molecules were located in difference Fourier maps. The O–H distances were normalized to 0.8492–0.8501 Å for $1 \cdot 12\text{H}_2\text{O}$, and the H-atoms were then allowed to ride on their parent with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{O})$. Calculations and graphics were performed with SHELXTL [26]. The highest peak and the deepest hole of $1 \cdot 12\text{H}_2\text{O}$ in the residual electron density are located 1.05 Å from Co2 and 0.73 Å from Co2, respectively. The crystallographic details are provided in table 1. Selected bond distances and angles are listed in table 2 for $1 \cdot 12\text{H}_2\text{O}$. Hydrogen bonds are listed in table S1.

3. Results and discussion

3.1. Synthesis

We have reported six heptanuclear clusters [3, 5(c)]. In order to study the function of CH_3O^- in the heptanuclear clusters, using H_2O to replace the CH_3OH , a double-bowl-like

Table 1. Crystallographic and experimental data for $1 \cdot 12\text{H}_2\text{O}$.

Formula	$\text{C}_{54}\text{H}_{90}\text{Cl}_2\text{Co}_7\text{N}_6\text{O}_{38}$
Formula mass	1914.73
Color, form	Red, block
T (K)	293(2)
Crystal system	Trigonal
Space group	$P\bar{3}c1$
a (Å)	14.239(1)
b (Å)	14.239(1)
c (Å)	23.271(3)
V (Å^3)	4086.2(7)
Z	2
D_{Calcd} (g cm^{-3})	1.556
μ (mm^{-1})	1.540
R_{int}	0.090
GOof	1.029
Completeness	99.6
F_{000}	1966
$R_1^a R_2^b [I > 2\sigma]$	0.0561
wR_2^b	0.2868
CCDC number	970331

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \frac{[\sum w(|F_o|^2 - |F_c|^2)^2]}{[\sum w(F_o^2)]^{1/2}}$$

Table 2. Selected bond lengths (Å) and angles (°) for $\mathbf{1} \cdot 12\text{H}_2\text{O}$.

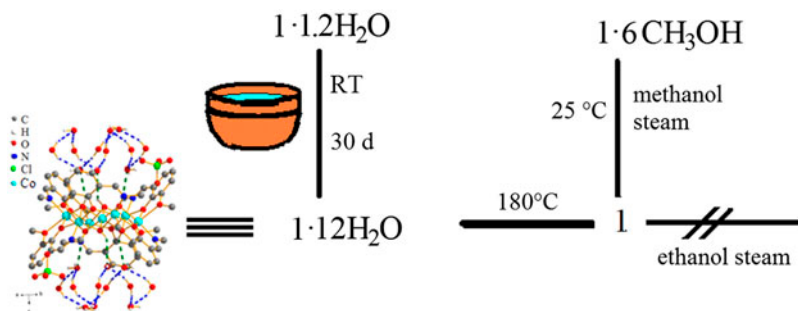
O1–Co1	2.090(8)	O1–Co2–O2 ⁱⁱ	80.4(3)
O2–Co2 ⁱ	2.009(9)	O1–Co2–O2	113.2(4)
O2–Co2	2.022(9)	O2 ⁱⁱ –Co2–O2	161.1(2)
O3–Co2 ⁱ	2.370(10)	O1–Co2–N1	100.2(5)
O1–Co2	2.008(9)	O2 ⁱⁱ –Co2–N1	102.2(5)
O1–Co2 ⁱⁱ	2.146(9)	O2–Co2–N1	88.6(5)
N1–Co2	2.080(13)	O1–Co2–O1 ⁱ	82.8(4)
Co1...Co2	3.114(1)	O2 ⁱⁱ –Co2–O1 ⁱ	92.7(4)
Co2...Co2 ⁱⁱⁱ	3.155(1)	O2–Co2–O1 ⁱ	76.9(4)
O1–Co1–O1 ⁱ	82.3(3)	N1–Co2–O1 ⁱ	165.2(5)
O1 ⁱⁱ –Co1–O1 ⁱ	97.7(3)	O1–Co2–O3 ⁱⁱ	151.1(4)
O1–Co1–O1 ^{iv}	180.0(6)	Co2–O1–Co1	98.9(4)
O2 ⁱⁱ –Co2–O3 ⁱⁱ	70.6(4)	Co1–O1–Co2 ⁱⁱ	94.6(3)
O2–Co2–O3 ⁱⁱ	95.2(4)	Co2–O1–Co2 ⁱⁱ	98.8(3)
N1–Co2–O3 ⁱⁱ	85.2(5)	Co2–O2–Co2 ⁱ	103.0(4)
O1 ⁱ –Co2–O3 ⁱⁱ	99.2(4)		

Notes: Symmetry codes: (i) $x-y, -y, 0.5-z$; (ii) $-y, -x, -0.5+z$; (iii) $y, -x+y, -z$; (iv) $y, x, 0.5-z$.

structure of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ was synthesized and not a disk-like structure as in the reference [3, 5 (c)]. In order to study the relationship between the water clusters and the core of $\mathbf{1} \cdot 12\text{H}_2\text{O}$, thermal gravimetric analysis of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ was measured between 25 and 900 °C. The results indicated that the core of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ is steady under 250 °C. Based on the result, $\mathbf{1} \cdot 12\text{H}_2\text{O}$ was heated to 180 °C at 5 °C min⁻¹ and nitrogen flow rate of 20 mL min⁻¹, and $\mathbf{1}$ can be obtained without the solvent water (figure S2). Because the surfaces have holes with diameter of 0.54 Å in the 1-D chain structure (figure S3), the water molecules can escape through the holes when it is in the air at room temperature. In fact, $\mathbf{1} \cdot 12\text{H}_2\text{O}$ was placed in the air at room temperature for 30 days. $\mathbf{1} \cdot 12\text{H}_2\text{O}$ becomes $\mathbf{1} \cdot 1.2\text{H}_2\text{O}$ which was determined through elemental analysis. $\mathbf{1} \cdot 6\text{CH}_3\text{OH}$ was formed when $\mathbf{1}$ was bathed in methanol gas for 5 days (figure S4). But $\mathbf{1} \cdot x\text{C}_2\text{H}_5\text{OH}$ ($x > 0$) cannot be obtained when $\mathbf{1}$ was bathed in ethanol gas. The results indicate that the methanol molecules can get through the holes but the ethanol molecules cannot (scheme 1).

3.2. Crystal structure

Single-crystal structure of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ features a double-bowl-like {Co₇} cluster (figure 1), belonging to the trigonal space group $P\bar{3}c1$. $\mathbf{1} \cdot 12\text{H}_2\text{O}$ consists of a μ_3 -OH bridged cationic



Scheme 1.

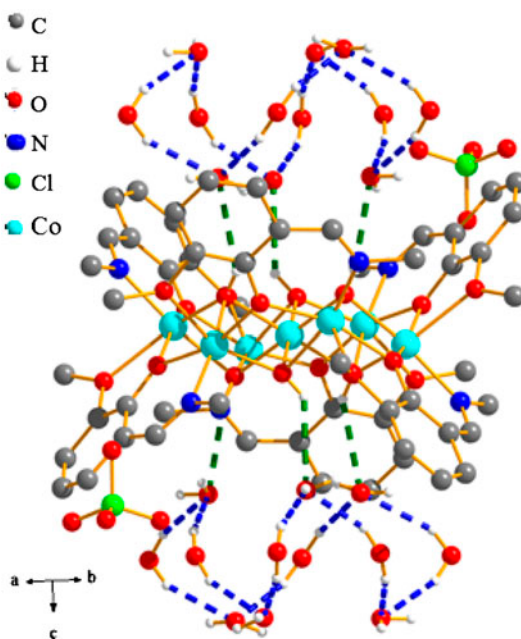


Figure 1. Structure of $\{[\text{Co}_7(\text{mmp})_6(\text{OH})_6] \cdot 12\text{H}_2\text{O}\}^{2+}$.

heptanuclear cluster $[\text{Co}_7(\text{L})_6(\text{OH})_6]^{2+}$, two counter anions (ClO_4^-), and a dodecamer water cluster. In the double-bowl-like structure of $1 \cdot 12\text{H}_2\text{O}$, six $\mu_2\text{-O}$ (phenoxo) groups bridge the six cobalt ions on the rim, which themselves are linked to the central cobalt through six $\mu_3\text{-OH}$ groups that act as “bottom” to form the double-bowl-like structure. The coordination geometry of the central cobalt ion (Co1) is slightly distorted octahedral with bond lengths of 2.090(8) Å (Co1–O1) and the O–Co1–O angles [*cis*-angles in the range of 82.3(3)°–97.7(3)°, but all *trans*-angles are 180.0(6)°]. Each cobalt ion on the rim (Co2) adopts a CoN_1O_5 configuration through coordination with mmp^{-1} and OH^{-1} groups. The Co2 ions have more distorted octahedral geometries [*cis*-angles range from 80.4(3)° to 113.2(4)° and *trans*-angles range from 151.1(4)° to 165.2(5)°] with the axial position elongated. Coordination bond lengths about Co2 are 2.008(9)–2.370(10) Å (table 2). The cobalt ions on the rim (Co2) and at the center (Co1) were all assigned to be the Co (II) ions, based on the valence sum calculation. The core of the cluster can be described as an almost planar Co_6 moiety with a crystallographically imposed S_6 -symmetry [Co2 and their centrosymmetric equivalents, deviation from the average plane ± 0.2938 Å] plus a Co1, which lies on the inversion center. It is noted that the structural motif belongs to the increasing {M7} family. Just as other {M7} clusters [3, 27–33], the Co–O–Co angles are in the range of 94.6(3)°–103.0(4)° and the adjacent Co–Co distances are 3.114(1)–3.155(1) Å.

A dodecamer water cluster has been observed in the double-bowl-like heptanuclear cobalt cluster $[\text{Co}_7(\text{mmp})_6(\text{OH})_6]_2 \cdot (\text{ClO}_4)_2 \cdot 12\text{H}_2\text{O}$ (figure 2, red ball) which further constructed a 1-D chain (figure 3). The geometrical parameters pertaining to the water cluster are collected in table S1. In the asymmetric unit of the dodecamer water cluster, O1w–O3w constitutes a part of the dodecanuclear water cluster. O3w is hydrogen bonded to O1w of this cluster, sideways, to fill the bowl in the discrete heptanuclear cation $[\text{Co}_7(\text{mmp})_6(\text{OH})_6]^{2+}$.

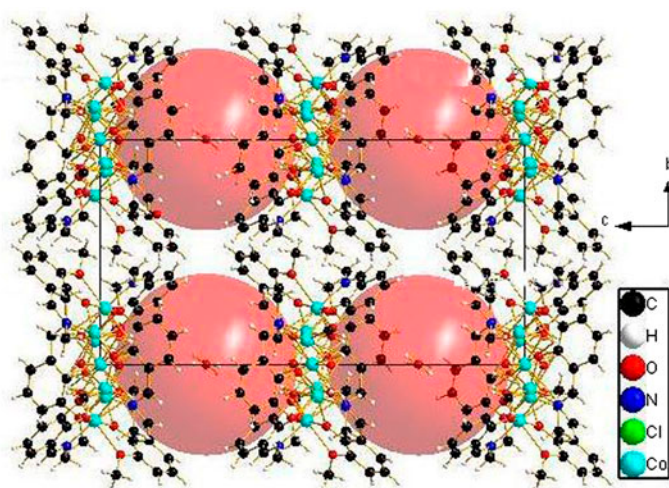


Figure 2. The large voids of $[\text{Co}_7(\text{mmp})_6(\text{OH})_6]^{2+}$ (red ball) (see <http://dx.doi.org/10.1080/00958972.2014.964221> for color version).

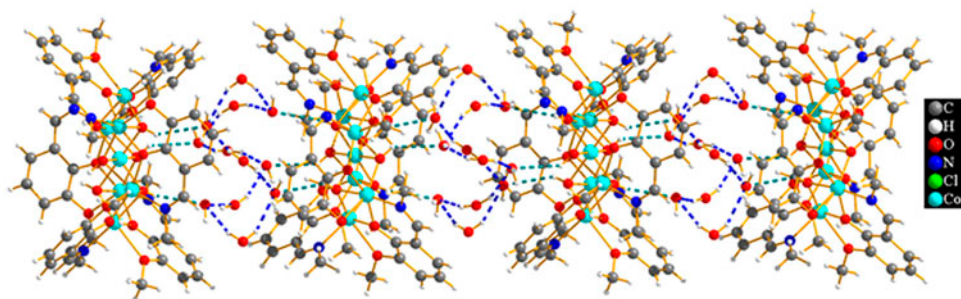


Figure 3. 1-D chain of $\{[\text{Co}_7(\text{mmp})_6(\text{OH})_6] \cdot 12\text{H}_2\text{O}\}^{2+}$.

Six O1–H1A···O3w weak hydrogen bonds hold the water cluster (figure 4, table S1). O2w and O3w are double donors and acceptors forming four-coordination hydrogen bonds. O1w in the water cluster forms two hydrogen bonds and also acts as a donor. The six O3w molecules are the acceptors to the μ_3 -OH (O1), which further stabilizes the dodecanuclear water cluster (figure 5). Thus, nine water molecules of the dodecanuclear water cluster exhibit four-coordination hydrogen bonds. Although each oxygen in an assembly of water molecules tends to achieve four coordination, hydrogen-bond-deficient water molecules are found on the surface of ice [34], and recent X-ray absorption spectroscopy and Raman scattering studies of liquid water also suggest that significant number of oxygen show less than four-coordinate hydrogen bonds [35]. Herein, O1w is located at the surface of the dodecanuclear water cluster model and the water molecules on the surface of ice or liquid water. Herein, we report the second example of a dodecanuclear water cluster [25], though some water clusters have already been reported [19–25].

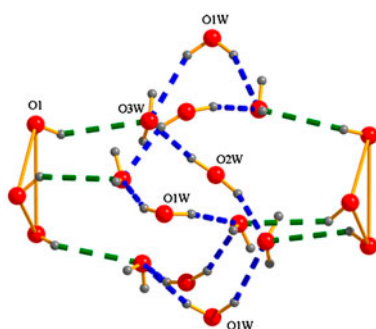


Figure 4. Relationship between bottom of double-bowl-like structure and water cluster of $1 \cdot 12\text{H}_2\text{O}$.

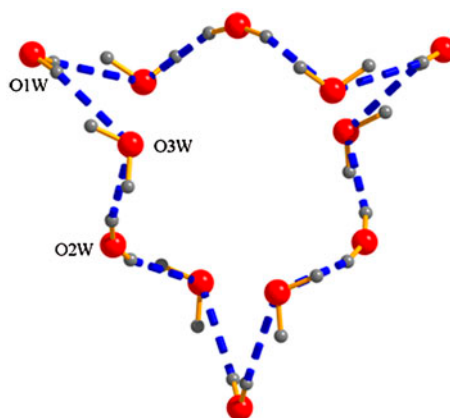


Figure 5. Dodecanuclear water cluster of $1 \cdot 12\text{H}_2\text{O}$.

3.3. PXRD patterns, thermogravimetric analysis, and IR

The microwave-synthesized samples of $1 \cdot 12\text{H}_2\text{O}$ and **1** which were derived from $1 \cdot 12\text{H}_2\text{O}$ through heating to 180 at $5\text{ }^\circ\text{C min}^{-1}$ have been characterized by PXRD (figure S5). The experimental PXRD patterns correspond well with the results simulated from the single-crystal data (herein, simulated PXRD of **1** comes from the single-crystal data of $1 \cdot 12\text{H}_2\text{O}$ but omitting 12 water molecules and refining), indicating the pure phase of $1 \cdot 12\text{H}_2\text{O}$ and **1**. The difference in reflection intensities between the simulated and experimental patterns was due to the variation in preferred orientation of the powder samples during the collection of the experimental PXRD data. A PXRD of $1 \cdot 12\text{H}_2\text{O}$ which was measured through varying temperatures from 25 to 300 $^\circ\text{C}$ indicates that the core of the $1 \cdot 12\text{H}_2\text{O}$ is steady until 250 $^\circ\text{C}$ (figure S6).

The interaction between the bowl and the water cluster is moderately strong (figure S7), as thermal gravimetric analysis with a 3.68 mg sample in nitrogen at a flow rate of 20 mL min^{-1} shows that weight loss occurs in stages beginning at 80 $^\circ\text{C}$ and loss of 11.89% corresponding to all of the water (calculated 11.28%) takes place under 180 $^\circ\text{C}$. Complete decomposition is achieved at $\sim 427\text{ }^\circ\text{C}$ (figure S8).

The IR spectrum of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ shows a broad band centered at 3443 cm^{-1} due to water molecules (figure S1). The IR spectra of ice show O–H stretching at 3220 cm^{-1} , whereas the stretching vibration in liquid water is at 3490 and 3280 cm^{-1} [36]. Hence, the water clusters in $\mathbf{1} \cdot 12\text{H}_2\text{O}$ show O–H stretching vibration similar to that of liquid water. Water clusters identified in other MOFs show O–H stretching at $3400\text{--}3500\text{ cm}^{-1}$ [6, 12]. Complex $\mathbf{1} \cdot 12\text{H}_2\text{O}$ showed strong bands at 1633 cm^{-1} which may be assigned to the $\nu(\text{C}=\text{N})$ stretching frequency [5(c)] and 1099 cm^{-1} to the stretching vibration of ClO_4^- .

3.4. Magnetic behavior properties for $\mathbf{1} \cdot 12\text{H}_2\text{O}$ and $\mathbf{1}$

The *dc* susceptibilities of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ were measured under an applied field of 1 kOe on a MPMS-XL7 SQUID magnetometer at temperatures ranging from 2 to 300 K. For $\mathbf{1} \cdot 12\text{H}_2\text{O}$, as shown in figure 6, the $\chi_{\text{M}}T$ value at 300 K is $21.86\text{ cm}^3\text{ KM}^{-1}$ per Co_7 molecule, which is much higher than the expected spin-only value of $13.1\text{ cm}^3\text{ KM}^{-1}$ for a non-interacting Co_7 unit assuming $g = 2.0$ [37] and $\chi_{\text{M}}T$ value of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ at room temperature is in accordance with that of other heptanuclear cobalt clusters ($\chi_{\text{M}}T$ value at room temperature ranges from 18.20 to $29.80\text{ \AA cm}^3\text{ KM}^{-1}$ (table S2) [3(b), 5(c), 28]). This can be explained by the orbital contribution to the magnetic moment of Co^{II} [38]. Upon cooling, the value slightly increases to a maximum of $40.44\text{ cm}^3\text{ KM}^{-1}$ at 2 K without any decrease at low temperature, indicating no antiferromagnetic interaction at any temperature higher than 2 K [39].

The temperature dependence of the reciprocal susceptibility χ_{M}^{-1} above 50 K follows the Curie–Weiss law [$\chi_{\text{M}} = C/(T - \theta)$] with Weiss constant of $\theta = 1.16\text{ K}$ and Curie constant of $C = 21.60\text{ cm}^3\text{ KM}^{-1}$ [figure S9(a), Supplemental data]. The positive Weiss constant indicates dominant intracluster ferromagnetic interaction between adjacent Co^{II} ions through the two kinds of oxygen exchange bridges ($\mu_3\text{-O-}$ and $\mu_2\text{-O-}$ bridge).

Further evidence of ferromagnetic coupling between $\text{Co}(\text{II})$ ions can be observed by variable-field magnetization as shown in figure S10(a). At low fields from 0 to 1 T, the magnetization of $\mathbf{1} \cdot 12\text{H}_2\text{O}$ sharply increases. Above 1 T, the magnetization slowly increases and saturates at $17.48\text{ N}\beta$.

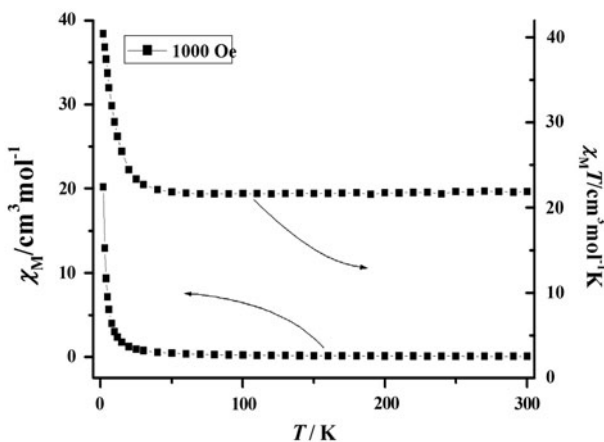


Figure 6. Plots of $\chi_{\text{M}}^{-1}T$ and $\chi_{\text{M}}T-T$ of $\mathbf{1} \cdot 12\text{H}_2\text{O}$.

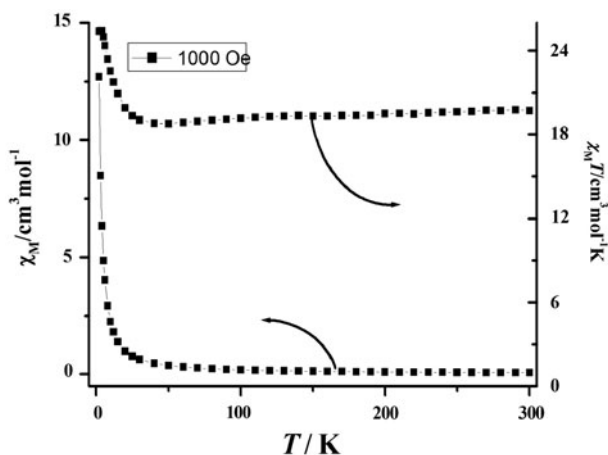


Figure 7. Plots of χ_M-T and $\chi_M T-T$ of **1**.

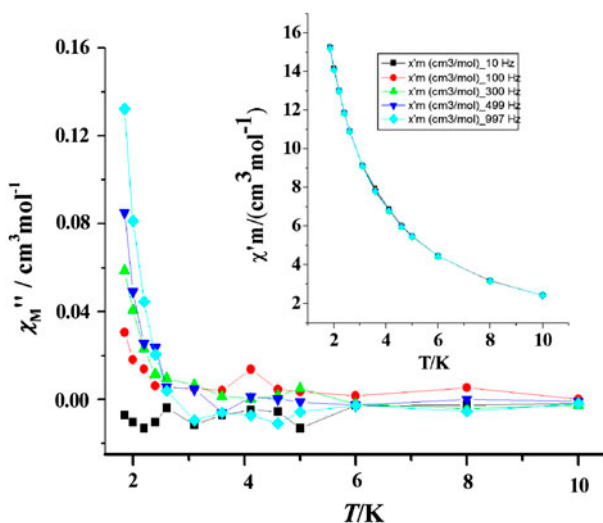


Figure 8. Plot of $\chi''-T$ and $\chi'-T$ of **1**.

Given the magnitude of χ_M , susceptibility studies were carried out in the 2–12 K range at frequencies of 10 and 997 Hz (figure S11). In- and out-of-phase ac susceptibility signals have no dependent frequency between 2 and 20 K. All of the magnetic results indicate that **1**·12H₂O does not show SMM behavior above 2 K.

The magnetic behavior of **1** is similar to that of **1**·12H₂O except that the room temperature and maximum $\chi_M T$ values are 19.70 and 25.41 cm³ KM⁻¹, respectively (figure 7). The temperature dependence of the reciprocal susceptibility (χ_M^{-1}) above 50 K follows the Curie–Weiss law [$\chi_M = C/(T-\theta)$] with a Weiss constant of $\theta = 0.77(1)$ K and a Curie constant of $C = 19.65(1)$ cm³ KM⁻¹ [figure S9(b), Supplementary material], indicating a

dominant intracluster ferromagnetic interaction. Further evidence of ferromagnetic coupling between Co (II) ions can be observed in the variable-field magnetization curve as shown in figure S10(b). At low fields from 0 to 1 T, the magnetization of **1** sharply increases. Above 1 T, the magnetization slowly increases and saturates at $14.30 N\beta$. But AC magnetic susceptibility is obviously different between **1** and **1**·12H₂O. Further magnetic measurements display the frequency-dependent AC magnetization as shown in figure 8, but the peak value has not appeared above 2 K. It may be a SMM under 2 K.

The magnetic behavior of **1** and **1**·12H₂O indicates that the hydrogen bonds among the clusters play a vital role in transferring the magnetic exchange effects.

4. Conclusion

Using microwave-assisted solvothermal method, we synthesized a double-bowl-like heptanuclear cluster with dodecanuclear water cluster in the bowl. **1** was formed through heating to 180 °C. The magnetic investigation shows that **1**·12H₂O and **1** display ferromagnetic interactions between cobalt ions. Moreover, **1** shows SMM behavior under 2 K. Magnetic behavior between **1** and **1**·12H₂O indicates that the hydrogen bonds play an important role in transferring the magnetic exchange effects.

Supplementary material

CCDC 970331 contain the supplementary crystallographic data for **1**·12H₂O. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif and also contain additional magnetic properties, IR, TG, XRD of **1**·12H₂O, and **1**. Relationship between the core of **1**·12H₂O and the water clusters, Space-filling plot of **1**·12H₂O.

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