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Study on the coordination of cyclopentanocucurbit[5,6]uril with Fe^{3+}, Co^{2+} and Ni^{2+} ions†

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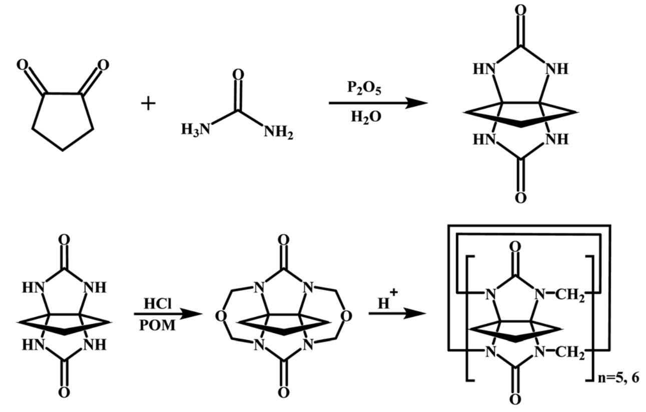
This paper reports the coordination of cyclopentanocucurbit[5]uril ($CyP_5Q[5]$) and cyclopentanocucurbit[6]uril ($CyP_6Q[6]$) with $Fe(ClO_4)_3$, $Co(ClO_4)_2$ and $Ni(ClO_4)_2$. Single crystal X-ray diffraction analysis shows the metal ions are directly coordinated with the portal of the cucurbit[*n*]uril to form a one-dimensional supramolecular chain or independent systems in the $CyP_5Q[5]@Fe(ClO_4)_3$, $CyP_5Q[5]@Co(ClO_4)_2$, $CyP_6Q[6]@Co(ClO_4)_2$ and $CyP_5Q[5]@Ni(ClO_4)_2$ complexes. In $CyP_6Q[6]@Fe(ClO_4)_3$, the metal ion is not directly coordinated with the cucurbit[*n*]uril portal, but after forming $Fe(H_2O)_6$, it interacts with the cucurbit[*n*]uril portal *via* a hydrogen bond. The $CyP_6Q[6]@Ni(ClO_4)_2$ complex is quite special; in this system, there are both metal ions directly coordinated with the cucurbit[*n*]uril portal and free on the outer surface of the cucurbit[*n*]uril.

1. Introduction

Cucurbit[*n*]uril (Q[*n*] or CB[*n*]),[1–13] a macrocyclic compound with an inner surface cavity and rich carbonyl portals, is a good electron donor due to the presence of a large number of carbonyl groups and therefore has a high density of electron clouds at its portal. Numerous experimental facts prove that Q[*n*] can coordinate with metal ions with different ionic radii such as alkali metals, alkaline earth metals, transition metals, lanthanide metals, *etc.* to form supramolecular assemblies in the presence of structural inducers through intermolecular interactions between water and amino groups, *etc.* and portal carbonyl oxygen of Q[*n*], which, however, is slightly soluble in water and organic solvents, limiting its scope of study. Alkyl-substituted Q[*n*]s are new Q[*n*]s prepared by reacting formaldehyde with alkyl-substituted glycoluril under acidic conditions; their solubility greatly improves compared with that of ordinary Q[*n*]s due to the electron-donating effect of alkyl groups, which increases the electron density of Q[*n*] portals and makes it relatively easy to coordinate with metal ions. So far, the main alkyl-modified Q[*n*]s reported are methyl-substituted Q[*n*]s,[14–16] cyclopentyl-substituted Q[*n*]s,[9,10,17–19] cyclohexyl-substituted Q[*n*]s[20–22] and cyclobutyl-substituted Q[*n*]s.[23]

In previous work, the coordination of CyP5Q[5] with alkali metal cations (A^+)[24] and alkaline earth metal cations (AE^{2+}),[25] CyP6Q[6] with alkaline earth metal cations (AE^{2+})[26] and lanthanides (Ln^{3+})[27] with $[ZnCl_4]^{2-}$ as an inducer are investigated. In 2019, Zhao *et al.* reported the coordination of cyclopentyl-substituted Q[*n*]s with Cu and Zn ions,[28] and in 2021, Ma *et al.* reported the supramolecular self-assembly of CyP5Q [5] with heavy metal ionic compounds ($CoCl_2$, $CrCl_3$, $HgCl_2$, $Pb(ClO_4)_2$) under acidic conditions,[29] extending the coordination studies of cyclopentyl-substituted Q[*n*]s with metal ions. In this paper, the cyclopentyl-substituted Q[*n*]s CyP5Q [5] and CyP6Q [6] are selected as organic ligands and the coordination modes with iron, cobalt and nickel ions are investigated, respectively, improving the model of the interaction of cyclopentyl-substituted Q[*n*]s with transition metals, from which the formed supramolecular framework structures are expected to have better application prospects in the fields of gas molecule adsorption, drug delivery, supramolecular chemistry and coordination chemistry.



Scheme 1 The synthesis process of cyclopentanocucurbit[5,6]uril.

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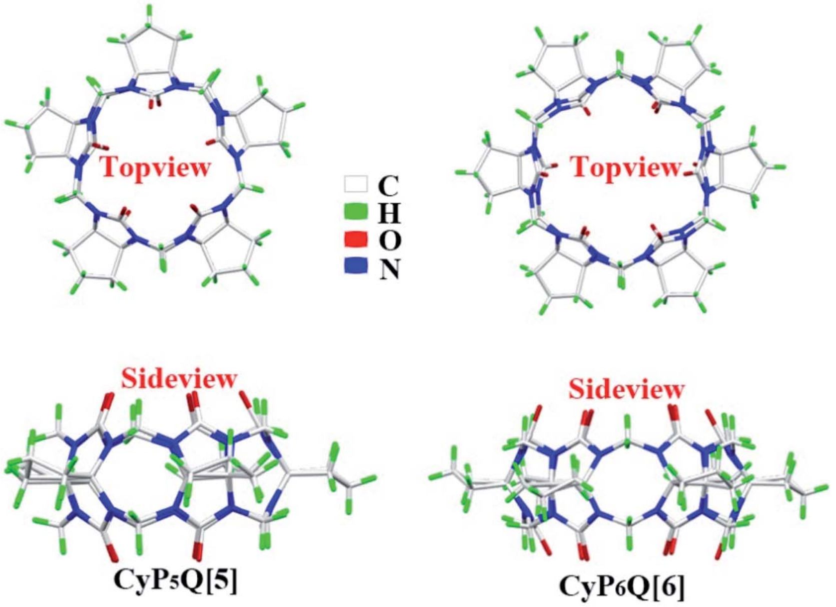

Fig. 1 The structures of $CyP_5Q[5]$ and $CyP_6Q[6]$.

2. Experimental section

2.1 General materials

All materials were reagent grade and used without any further purification. Cyclopentanocucurbit[5]uril and cyclopentanocucurbit[6]uril was prepared and purified in accordance with a literature method[9,10] (as shown in Scheme 1) and its structure is shown in Fig. 1.

2.2 Synthesis of the complexes 1–6

Preparation of complex **1:** a mixture of $CyP_5Q[5]$ (10 mg, 9.73 μmol) and $Fe(ClO_4)_3 \cdot H_2O$(15.5 mg, 41.6 μmol) in 3 mL of 70% (v/v) formic acid aqueous solution was heated until dissolution. The solution was heated and stirred for 5–10 min in a water bath at 35 °C. The resulting solution was allowed to stand at room temperature for 7–10 d to obtain single crystals of

Table 1 The crystal structure parameters of complex **1–3**

Complex	**1**	**2**	**3**
Empirical formula	$C_{90}H_{108}Cl_4Fe_2N_{40}O_{40}$	$C_{90}H_{108}Cl_3Co_2N_{40}O_{36}$	$C_{45}H_{60}Cl_2NiN_{20}O_{23}$
Formula weight	2643.66	2550.37	1378.74
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P1$	$P1$	$P2_1/n$
a [Å]	15.734(6)	15.667(4)	11.981(4)
b [Å]	19.695(7)	19.553(5)	32.393(10)
c [Å]	23.581(9)	23.434(6)	16.243(5)
α [°]	65.774(9)	66.076(7)	90
β [°]	81.704(9)	81.367(7)	98.681(10)
γ [°]	84.656(9)	84.437(7)	90
V [Å^3]	6590(4)	6482(3)	6232(3)
Z	2	2	4
D_c (g cm $^{-3}$)	1.332	1.307	1.470
T [K]	296.15	296.15	296.15
F(000)	2736	2642	2864
μ [mm $^{-1}$]	0.391	0.404	0.489
Data/params	23 242/1737	22 835/1592	10 988/937
R_{int}	0.0903	0.0801	0.0895
R [I > 2σ(I)]^a	0.0779	0.0780	0.0884
wR [I > 2σ(I)]^b	0.2147	0.2206	0.2253
R (all data)	0.1460	0.1297	0.1287
wR (all data)	0.2465	0.2499	0.2496
GOF on F^2	1.042	1.031	1.031

[a] Conventional R on $Fhkl$: $\sum||F_o| - |F_c||/\sum|F_o|$. [b] Weighted R on $|Fhkl|2$: $\sum[w(F_o{}^2 - F_c{}^2)2]/\sum[w(F_o{}^2)2]1/2$.

Table 2 The crystal structure parameters of complex **4–6**

Complex	**4**	**5**	**6**
Empirical formula	$C_{54}H_{84}Cl_6Fe_2N_{24}O_{48}$	$C_{54}H_{68}Cl_2CoN_{24}O_{24}$	$C_{54}H_{82}Cl_4Ni_2N_{24}O_{39}$
Formula weight	2161.80	1567.15	1950.65
Crystal system	Trigonal	Triclinic	Triclinic
Space group	$R3$	$P1$	$P1$
a [Å]	19.654(4)	14.193(2)	21.326(5)
b [Å]	19.654(4)	16.298(2)	22.267(6)
c [Å]	20.369(7)	17.110(3)	22.325(6)
α [°]	90	79.312(5)	92.482(7)
β [°]	90	74.581(6)	97.727(8)
γ [°]	120	73.497(5)	97.905(6)
V [Å^3]	6814(4)	3632.2(10)	10 385(5)
Z	3	2	4
D_c (g cm^{-3})	1.581	1.433	1.248
T [K]	296.0	273.15	273.15
F(000)	3342	1626	4040
μ [mm $^{-1}$]	0.605	0.401	0.549
Data/params	2680/217	18 022/969	33 444/2245
R_{int}	0.1299	0.0526	0.1067
R [$I > 2\sigma$(I)]^a	0.1067	0.0792	0.1370
wR [$I > 2\sigma$(I)]^b	0.3438	0.2432	0.3692
R (all data)	0.1252	0.1044	0.2432
wR (all data)	0.3616	0.2678	0.4286
GOF on F^2	1.704	1.033	1.165

^{a} Conventional R on $Fhkl$: $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} Weighted R on $|Fhkl|2$: $\sum[w(F_o{}^2 - F_c{}^2)2]/\sum[w(F_o{}^2)2]1/2$.

$C_{90}H_{108}Cl_4Fe_2N_{40}O_{40}$ ref. 1 (32.5% yield), using a similar synthetic procedure gave single crystals of $C_{90}H_{108}Cl_3Co_2N_{40}O_{36}$ ref. 2 (38.4% yield), $C_{45}H_{60}Cl_2NiN_{20}O_{23}$ ref.[3] (42.3% yield); preparation of complex **4**: a mixture of CyP$_6$Q[6] (10 mg, 8.08 μmol) and $Fe(ClO_4)_3 \cdot H_2O$ (15.5 mg, 41.6 μmol) in 3 mL of 70% (v/v) formic acid aqueous solution was heated until dissolution. The solution was heated and stirred for 5–10 min in a water bath at 35 °C. The resulting solution was allowed to stand at

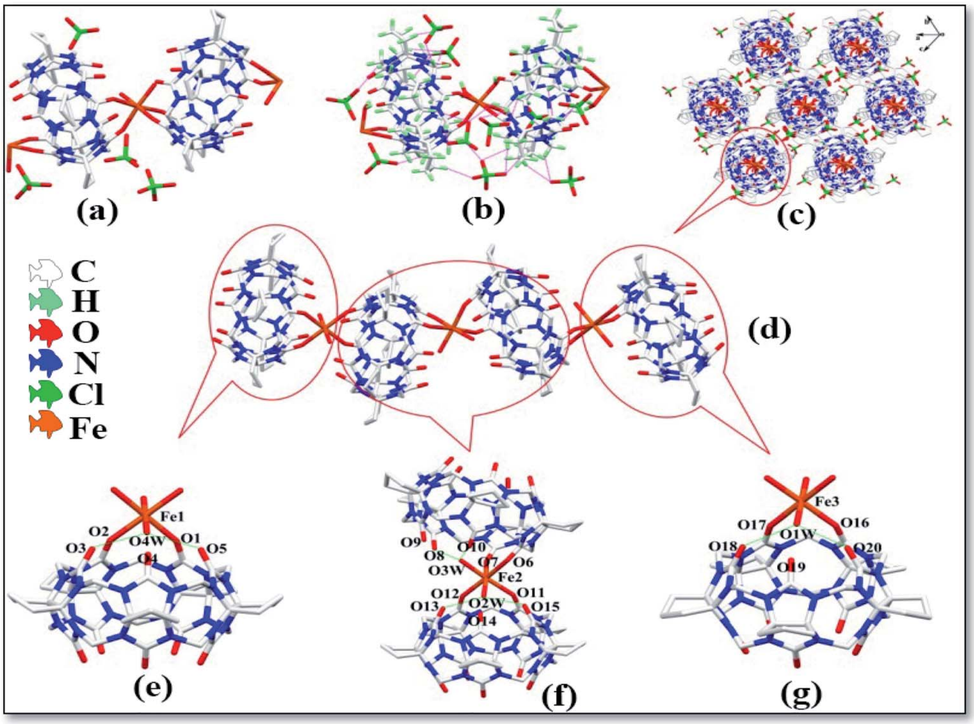

Fig. 2 Structure of complex **1**: (a) asymmetric unit, (b) ion–dipole interactions, (c) stacking diagram, (d) one-dimensional supramolecular chain and (e–g) hydrogen atoms bond interactions.

room temperature for 7–10 d to obtain single crystals of $C_{54}H_{84}Cl_6Fe_2N_{24}O_{48}$ ref. 4 (35.8% yield), using a similar synthetic procedure gave single crystals of $C_{54}H_{68}Cl_2CoN_{24}O_{24}$ ref. 5 (40.4% yield) and $C_{54}H_{82}Cl_4Ni_2N_{24}O_{39}$ ref. 6 (36.2% yield), respectively.

2.3 Crystal structure determination

A crystal with the appropriate size and transparency was selected and fixed on a glass probe with using petroleum jelly for X-ray single crystal diffraction analysis on a Bruker D8 Venture X-ray single crystal diffractometer in ω-scan mode using graphite to monochromatize the Mo-Kα rays ($\lambda = 0.71073$ Å, $\mu = 0.828\ \text{mm}^{-1}$). The crystal data were collected and Lorentz polarization and absorption correction carried out. SHELXT-14 and SHELXL-14 program packages were used for structural analysis and full matrix least squares refinement. All non-hydrogen atoms atoms were anisotropically refined using the analytical expression of the neutral atom scattering factor and combined with anomalous dispersion correction. The SQUEEZE program in the PLATON package was used to delete some of the disordered solvent molecules. The X-ray crystallographic data for structures reportaled in this study have been deposited in the Cambridge Crystallographic Data Center under accession numbers CCDC: 2 126 692,[1] 2 126 694,[2] 2 126 707,[3] 2 126 712,[4] 20 126 713 ref. 5 and 2 126 724.[6] These data can be obtained free of charge *via* **https://www.ccdc.cam.ac.uk/datarequest/cif**. The crystal parameters, data acquisition conditions, and parameters of the complexes **1–3** are listed in Table 1 and **4–6** are listed in Table 2.

3. Results and discussion

3.1 Description of the crystal structure of complexes 1-6

The asymmetric unit of complex **1** contains two $CyP_5Q[5]$, three Fe^{3+} ions, four coordination water molecules and four free perchlorate ions, as shown in Fig. 2a. The free perchlorate oxygen atoms and methylene hydrogen atoms atoms on the outer surface of $CyP_5Q[5]$ were connected *via* ion–dipole interactions (Fig. 2b), the ion–dipole interactions distances range from 2.272 Å to 2.689 Å. The Fe^{3+} ion of the complex has a distorted octahedral coordination configuration; each Fe^{3+} ion is coordinated to four carbonyl oxygen atoms and two water molecules in $CyP_5Q[5]$. The length of the coordination bond between Fe^{3+} and the $CyP_5Q[5]$ carbonyl oxygen atom is in the range of 2.105–2.134 Å, the coordination bond length between Fe^{3+} and oxygen atom of the coordinated water molecule is in the range of 2.057–2.093 Å, the bond angle around Fe^{3+} ion

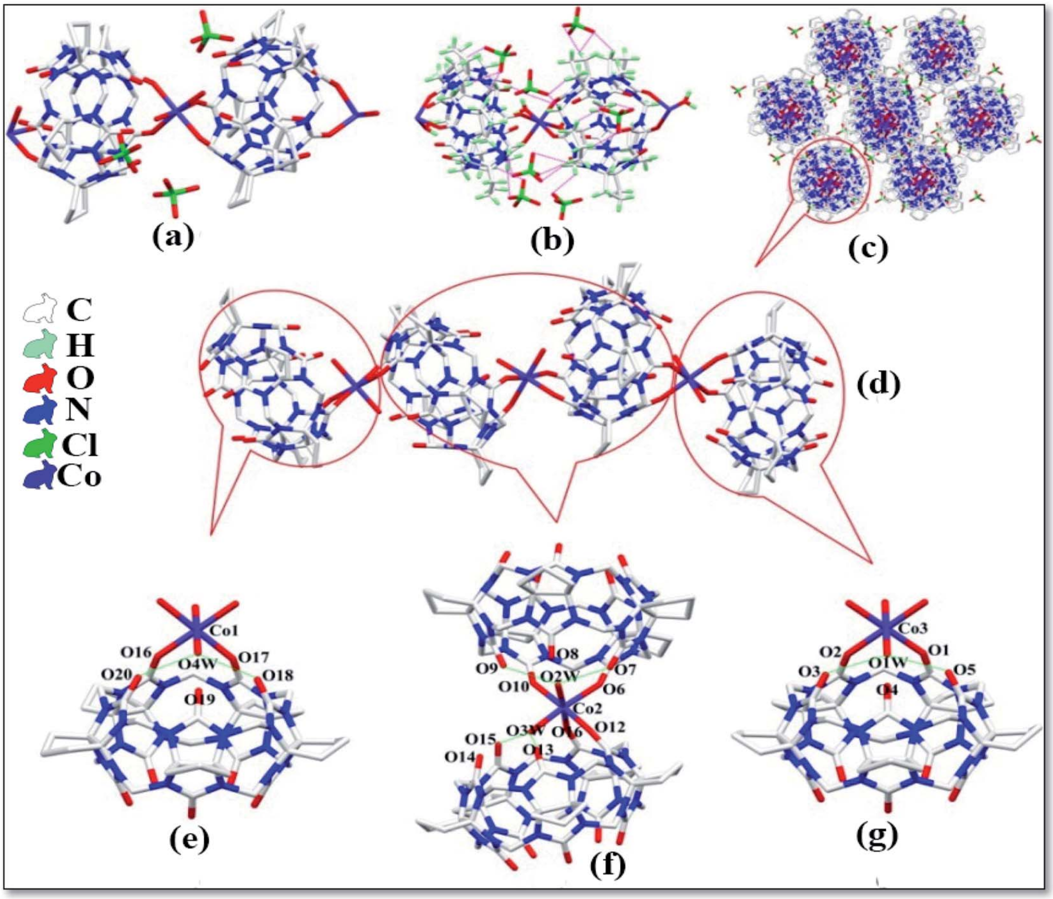

Fig. 3 Crystal structure of complex **2**: (a) asymmetric unit, (b) ion–dipole interactions, (c) stacking diagram, (d) one-dimensional supramolecular chain and (e–g) hydrogen atoms bond interactions.

ranges from 83.79 to 93.72°. The $CyP_5Q[5]$ was coordinated and bridged by two Fe^{3+} ions through the oxygen atoms of the two portal carbonyl groups to form a one-dimensional supramolecular chain with alternating V- and Z-types (Fig. 2d). The distances between Fe_1–Fe_2, Fe_2–Fe_3 and Fe_1–Fe_3 in the one-dimensional supramolecular chain are 9.157, 9.680 and 18.761 Å, respectively. The angles between the two $CyP_5Q[5]$ molecules connected to Fe_1, Fe_2 and Fe_3 are 0, 29.21 and 0°, respectively. There is also a hydrogen atoms bond formed between the water molecules participating in the coordination bond and the carbonyl oxygen atom at the end of the cucurbit[*n*]uril. Fig. 2c is a three-dimensional stacking diagram of complex **1**.

The asymmetric unit of complex **2** is shown in Fig. 3a, which contains two $CyP_5Q[5]$, three Co^{2+} ions, four coordinated water molecules and three free perchlorate counter ions. The oxygen atoms of the free perchlorate and methylene hydrogen atoms atom on the outer surface of $CyP_5Q[5]$ are connected *via* ion–dipole interactions (Fig. 3b), the ion–dipole interactions distances range from 2.405 Å to 2.689 Å. The Co^{2+} ion of the complex has a distorted octahedral coordination configuration, each Co^{2+} ion is coordinated with the four carbonyl oxygen atoms and two water molecules of the cucurbit[*n*]uril. The coordinate bond length between Co^{2+} and the $CyP_5Q[5]$ carbonyl oxygen atom is in the range of 2.077–2.102 Å, the bond angle around Co^{2+} ion ranges from 85.06 to 95.19°, and the coordinate bond length to the coordinated water molecule oxygen is in the range of 2.017–2.059 Å. The cucurbit[*n*]uril is coordinated and bridged by two Co^{2+} ions *via* the oxygen atoms of two portal carbonyl groups to form a one-dimensional supramolecular chain with alternating V- and Z-types (Fig. 3d). The distances between Co1–Co_2, Co_2–Co_3 and Co_1–Co_3 in the one-dimensional supramolecular chain are 9.588, 9.053 and 18.567 Å, respectively. The angles between the two $CyP_5Q[5]$ connected to Co_1, Co_2 and Co_3 are 0, 29.23 and 0°, respectively. There is also a hydrogen atoms bond between the water molecules participating in the coordination bond and the carbonyl oxygen atom at the end of $CyP_5Q[5]$. Fig. 3c is a three-dimensional stacking diagram of complex **2**.

The asymmetric unit structure of complex **3** is shown in Fig. 4a, which contains one $CyP_5Q[5]$, one Ni^{2+} ion, four coordinated water molecules, one free water molecule and two free perchlorate ions. Each $CyP_5Q[5]$ is surrounded by five free perchlorate counter ions, which are connected *via* ion–dipole interactions; the mode of action is shown in Fig. 4b, the ion–dipole interactions distances range from 2.333 Å to 2.698 Å. The

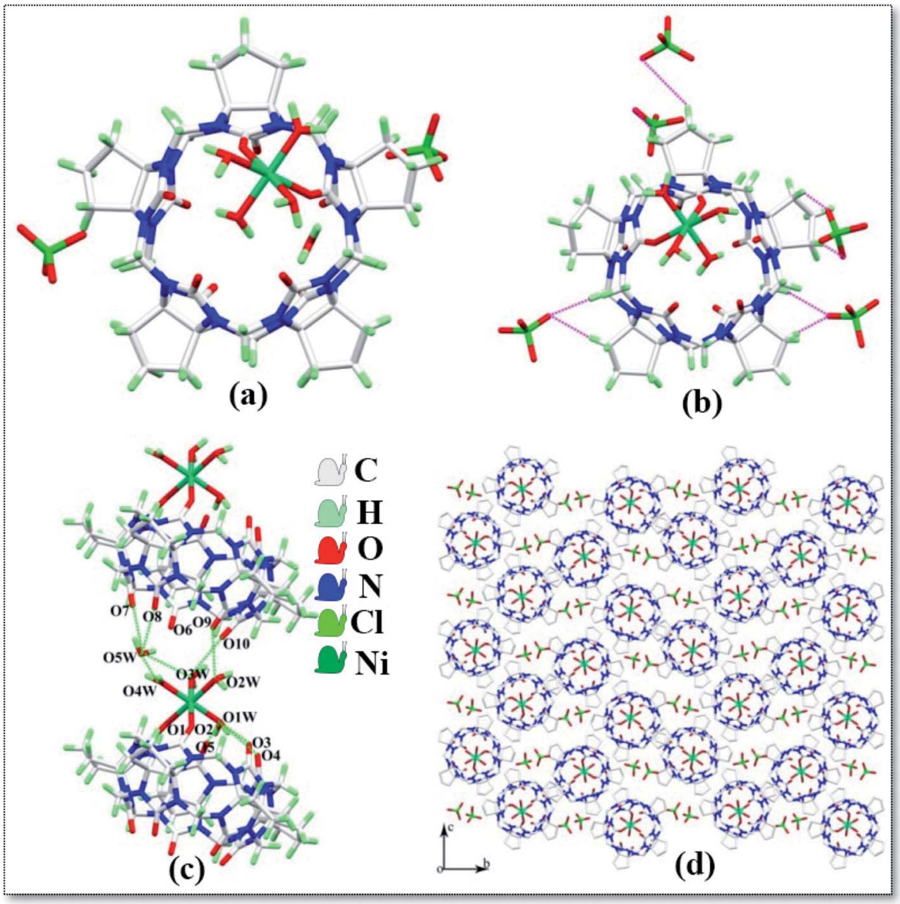

Fig. 4 Crystal structure of complex **3**: (a) asymmetric unit; (b) ion–dipole interactions, (c) hydrogen atoms bond interactions and (d) stacking diagram viewed along the *a*-axis.

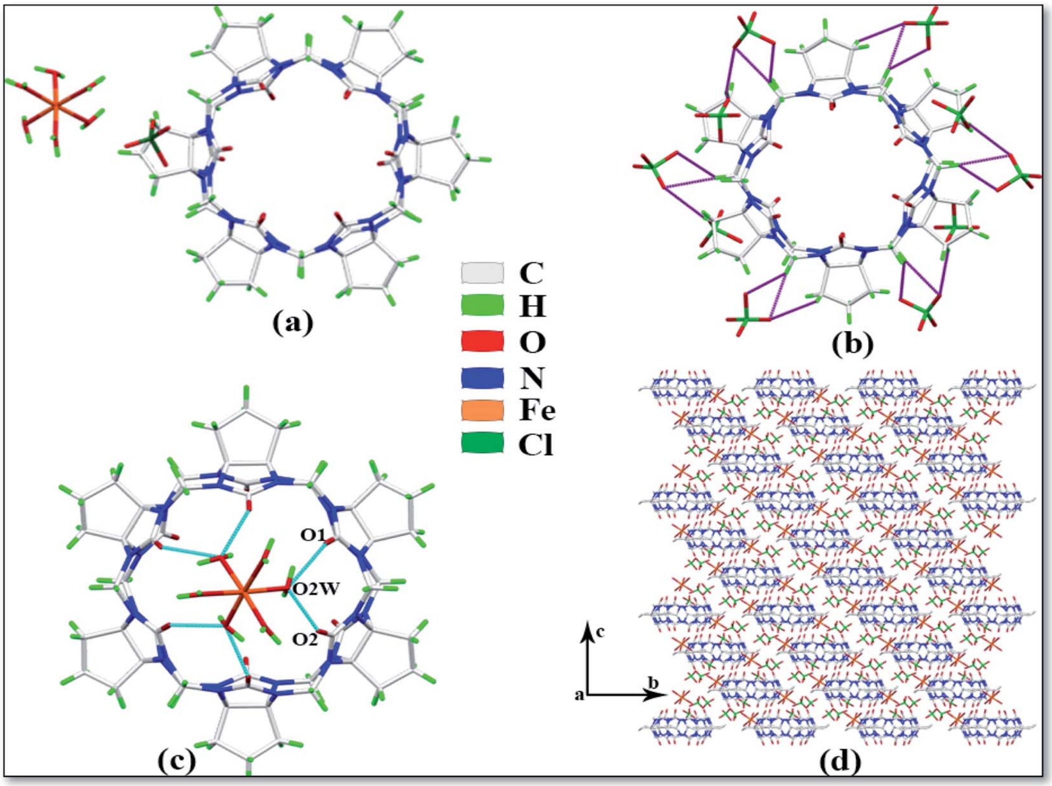

Fig. 5 Crystal structure of complex 4: (a) Asymmetric unit, (b) ion–dipole interactions, (c) hydrogen atoms bond interactions and (d) stacking diagram viewed along the *a*-axis.

Ni^{2+} ion of the complex has a twisted octahedral coordination configuration and each Ni^{2+} ion is coordinated to two carbonyl oxygen atoms and four water molecules at one portal carbonyl group of the cucurbit[*n*]uril. The length of the coordination bond between Ni^{2+} ion and $CyP_5Q[5]$ carbonyl oxygen atom is 2.085–2.091 Å, the length of coordination bond with the coordinated water molecule oxygen atom is 2.018–2.067 Å and the bond angle around Ni^{2+} ranges from 86.20 to 95.49°. There is a hydrogen atoms bond formed between the water molecules participating in the coordination bond and the carbonyl oxygen atom at the portal of $CyP_5Q[5]$, the carbonyl oxygen atom at the lower portal of the other $CyP_5Q[5]$ is connected *via* hydrogen atoms bonds, and the free water molecules are bridged and coordinated *via* hydrogen atoms bonding between the water molecule and carbonyl oxygen atom of the other $CyP_5Q[5]$ portal (Fig. 4c). Fig. 4d is a stacking diagram of the complex **3** viewed along the *a*-axis.

The asymmetric unit of complex **4** is shown in Fig. 5a, which contains one $CyP_6Q[6]$, one Fe^{3+} ion, six coordinated water molecules, and one free perchlorate ion. Each $CyP_6Q[6]$ is surrounded by ten free perchlorate counter ions, which are connected *via* ion–dipole interactions; the mode of action is shown in Fig. 5b, the ion–dipole interactions distances range from 2.641 Å to 2.719 Å. The Fe^{3+} ion of the complex has an octahedral coordination configuration; each Fe^{3+} ion is coordinated to six water molecules and the coordination bond length with the coordinated water molecule oxygen atom is 1.968–1.999 Å, and the bond angle around the Fe^{3+} ion ranges from 89.31 to 92.74°. There is a hydrogen atoms bond formed between the water molecule participating in the coordination bond and the carbonyl oxygen atom at the portal of the cucurbit[*n*]uril, which is connected with the carbonyl oxygen atom at the lower port of the other cucurbit[*n*]uril *via* a hydrogen atoms bond. Unlike other complexes, Fe^{3+} is not directly coordinated with the cucurbit[*n*]uril portal. The free water molecules bridge the coordinated water molecule and the carbonyl oxygen atom in the other cucurbit[*n*]uril portal *via* hydrogen atoms bonding (shown in the blue curve in Fig. 5c), the specific performance is O_1–O_2W and O_2–O_2W, and the distance between them is 2.606 and 2.573 Å respectively. Fig. 5d is the stacking diagram of complex **4** viewed along the *a*-axis. It can be seen from the figure that there are obvious gaps between the cucurbit[*n*]urils and the $ClO4^-$ counter ions are dispersed in these gaps.

The asymmetric unit of complex **5** is shown in Fig. 6a, which contains one $CyP_6Q[6]$, one Co^{2+} ion, four coordinated water molecules and two free perchlorate ions. The Co^{2+} ion of the complex has a twisted octahedral coordination configuration. Each Co^{2+} ion is coordinated with two carbonyl oxygen atoms and four water molecules at one portal of the cucurbit[*n*]uril and the Co^{2+} ion is coordinated with the carbonyl oxygen atom of the cucurbit[*n*]uril. The coordination bond length is 2.081–2.179 Å, the coordination bond length with the coordinated water molecule oxygen is 2.023–2.108 Å and the bond angle around the Co^{2+} ion ranges from 85.77 to 102.61°. There is

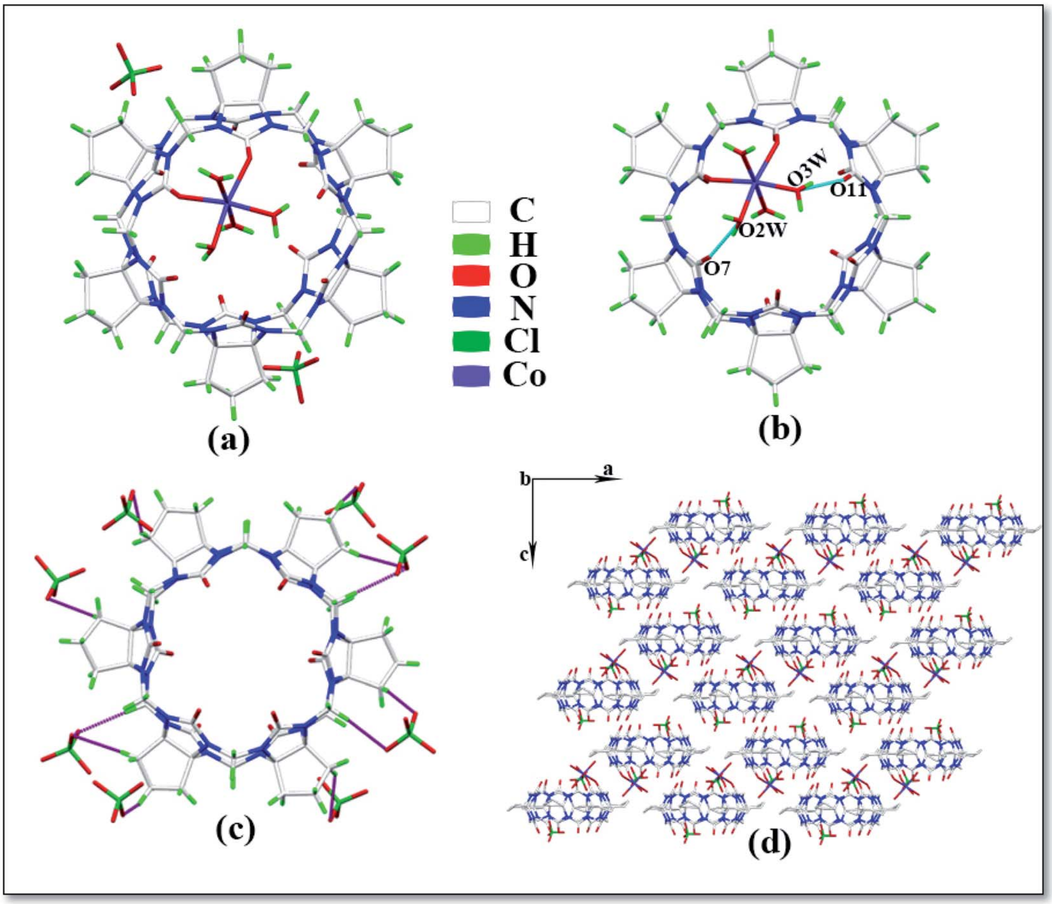

Fig. 6 Crystal structure of complex **5**: (a) asymmetric unit, (b) ion–dipole interactions, (c) hydrogen atoms bond interactions and (d) stacking diagram viewed along the *b*-axis.

a hydrogen atoms bond formed between the water molecule participating in the coordination bond and the carbonyl oxygen atom at the portal of the cucurbit[*n*]uril, which is connected with the carbonyl oxygen atom at the lower portal of the other CyP$_6$Q[6] *via* a hydrogen atoms bond. The free water molecule bridges the coordinated water molecule and carbonyl oxygen atom of another cucurbit[*n*]uril portal *via* hydrogen atoms bonding (Fig. 6b), which are specifically expressed as O$_7$–O$_2$W and O$_{11}$–O$_3$W, and the distance between them is 2.699 and 2.788 Å, respectively. Each CyP$_6$Q[6] is surrounded by eight free perchlorate ions, which are connected *via* ion–dipole interactions, the ion–dipole interactions distances range from 2.332 Å to 2.673 Å. The mode of action is shown in Fig. 6c. Fig. 6d is the stacking diagram of complex **5** viewed along the *b*-axis.

The asymmetric unit structure diagram of complex **6** is shown in Fig. 7a, which contains two CyP$_6$Q[6], four Ni^{2+} ions, twenty coordinated water molecules, two free water molecules and eight free ClO4$^-$ ions. Among the four Ni^{2+} ions in this complex, two Ni^{2+} ions are directly coordinated with the carbonyl oxygen atom of the CyP$_6$Q[6] portal and the Ni^{2+} ion of the complex has a distorted octahedral coordination configuration. Each Ni^{2+} ion is coordinated with two carbonyl oxygen atoms and four water molecules at one portal of the CyP$_6$Q[6]. The coordination bond length between Ni^{2+} and the carbonyl oxygen atom of CyP$_6$Q[6] is 2.080–2.087 Å, which is coordinated with the coordinated water molecule oxygen atoms. The position bond length is 1.951–2.105 Å and the bond angle around the Ni^{2+} ion is in the range of 77.88–96.21°. The other two Ni^{2+} ions are coordinated with six water molecules, but due to the forces between the CyP$_6$Q[6] molecules, these two Ni^{2+} ions are not in a regular coordination configuration; it is a twisted octahedral configuration like the two Ni^{2+} ions participating in the coordination bond, the coordination bond length between the Ni^{2+} ion and coordinated water molecule oxygen atom is 1.951–2.105 Å, and the bond angle around the Ni^{2+} ion is 77.88–96.21°. There is a ClO4$^-$ counter ion contained in the cavity of CyP$_6$Q[6], which is fixed in the cavity of CyP$_6$Q[6] *via* ion–dipole interactions and hydrogen atoms bonding, and the remaining ClO$_4$$^-$ ions are passed through the ion and the dipole effect surrounds the cucurbit[*n*]uril (Fig. 7b), the ion–dipole interactions distances range from 2.523 Å to 2.707 Å. Fig. 7c shows the cucurbit[*n*]urils are mainly connected *via* hydrogen atoms bonding in this complex. The coordinated water molecules on the Ni^{2+} ion that are not directly coordinated with CyP$_6$Q[6] and the CyP$_6$Q[6] molecules are directly connected. The coordinated water molecule on the coordinated Ni^{2+} ion, acts as a bridging

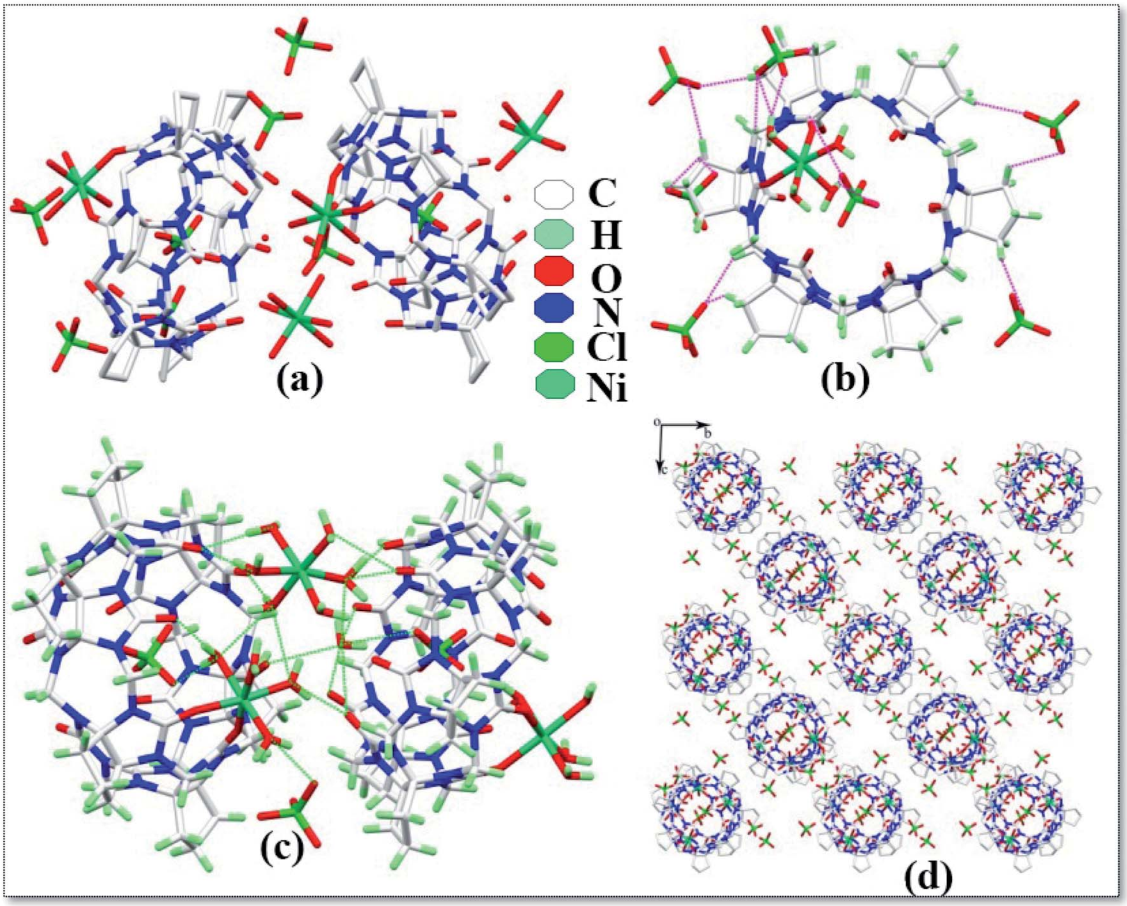

Fig. 7 Crystal structure of complex **6**: (a) asymmetric unit, (b) ion–dipole interactions, (c) hydrogen atoms interactions and (d) stacking diagram viewed along the *a*-axis.

compound connecting the CyP$_6$Q[6] molecules. There are also hydrogen atoms bonds formed between the free water molecules and ClO4$^-$ ions in the cavity and coordinated water molecules and the carbonyl oxygen atom of CyP6Q[6]. Fig. 7d is the stacking diagram of the complex viewed along the *a*-axis. It can be clearly seen from the figure that there are obvious gaps between the CyP$_6$Q[6] molecules and the ClO4$^-$ counter ions are dispersed in these gaps.

4. Conclusions

In this article, we reported the coordination of cyclopentanocucurbit[5]uril(CyP$_5$Q[5]) and cyclopentanocucurbit[5]uril(CyP$_6$Q[6]) with Fe(ClO$_4$)$_3$, Co(ClO$_4$)$_2$ and Ni(ClO$_4$)$_2$. In complex **1**, **2**, **3** and **5**, the metal ion is directly coordinated with the portal of the cucurbit[*n*]uril to form a one-dimensional supramolecular chain system or independent system; in complex **4**, the metal ion is not directly coordinated with the cucurbit[*n*]uril portal, but after forming Fe(H$_2$O)$_6$, it interacts with the cucurbit[*n*]uril port *via* hydrogen atoms bonding. Complex **6** is quite special. In this system, there are both metal ions directly coordinated with the cucurbit[*n*]uril portal and metal ions free on the outer surface of the cucurbit[*n*]uril. This further improved the gaps in the study of the complexes of cyclopentyl-substituted cucurbit[*n*]urils with metal ions, and has laid a theoretical foundation for the application of cucurbit[*n*]urils in the adsorption of metal ions.

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Ethics statement

No related experiments.

Conflicts of interest

The authors declare on conflict of interest.

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