

Discrete $\{Ni_{40}\}$ Coordination Cage: A Calixarene-Based Johnson-Type (J_{17}) Hexadecahedron

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Supporting Information

ABSTRACT: We report a Johnson hexadecahedral coordination cage, constructed via 10 Ni_4 -*p*-*tert*-butylthiacalix[4]arene (Ni_4 -TC4A) units as vertices and 16 5-(pyridin-4-yl)isophthalate (PIP) ligands as tiles. It features a gyroelongated square bipyramidal geometry, equivalent to two square pyramids pillared by a square antiprism, a J_{17} Johnson solid. Remarkably, the cage compound exhibits a much higher uptake capacity of C_3H_8 than CH_4 , representing a promising material for separation of these two gases. In contrast, Co_4 -TC4A units are linked by PIP ligands and rare $\{Co_4O_4Cl_2\}$ clusters, providing a one-dimensional bamboo stick-like polymer.

Metal–organic molecular architectures have been investigated extensively due to their fascinating structures, unique physical and chemical properties, and intriguing applications in supramolecular chemistry and material science.¹ The design and construction of such supramolecular assemblies draw inspiration from not only high-symmetry biological systems but also geometric entities.² The structure of molecular architectures can be controlled by selecting metal ions or metal clusters with distinct coordination geometries and organic ligands with various shapes and bridging angles.^{1k,3} Beside prisms and antiprisms, Archimedean and platonic solids are commonly found for these architectures, usually assembled by symmetric building units. In contrast, building non-Archimedean/platonic solids requires less symmetric linkers.^{1l} Among the nonclassical architectures, the discrete metal–organic Johnson solids are scarcely observed. Only two types of Johnson solids have been reported.⁴ Two metal–organic hendecahedra were obtained through the self-assembly of paddlewheel Cu_2 units and mixed ditopic linkers with 90° and 120° bend angles. They belong to the J_{35} -type Johnson solid with the geometry of elongated triangular orthobicupola.^{4a} Similarly, in the combination of mixed ditopic linkers with 180° and 120° bend angles, two indium-based metal–organic dodecahedra were synthesized. They exhibit an elongated bipyramidal configuration, corresponding to a J_{15} -type Johnson solid.^{4b}

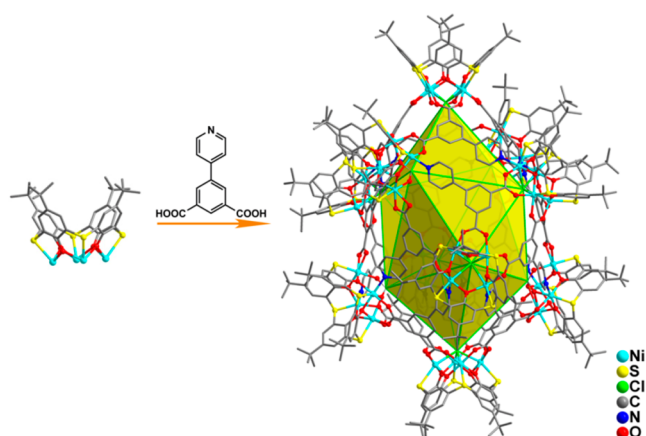
Calixarenes are versatile building blocks for constructing polynuclear metal–organic compounds, as they are available via facile syntheses and their functionality can be adjusted by changing bridging atoms in their lower rim.⁵ A variety of calixarene- and resorcinarene-based nanoscale coordination cages with well-defined shapes and sizes were prepared via metal-seamed self-assembly.⁶ Thiacalix[4]arenes (H_4 TC4A), a derivative of calix[4]arenes, react with metal ions to form a shuttlecock-like M_4 -TC4A unit, which acts as a four-connected secondary building unit (SBU). M_4 -TC4A SBUs, serving as metal cluster nodes, coordinate with auxiliary organic linkers to form large discrete molecular entities at nanoscopic scales or extended network structures in multiple dimensions.^{7,8} It is common that metal–organic cages with high-symmetry are built from more symmetrical components. For example, various tricarboxylate linkers in D_{3h} symmetry were able to connect M_4 -TC4A units in C_{4v} point group via an [8 + 6] condensation, forming a series of octahedral coordination cages with tunable size in nanometer scales.^{8b} We reasoned that the less symmetric, nonclassical polyhedra like Johnson solids could be prepared using organic linkers having lower symmetry. We therefore tested the ligand 5-(pyridin-4-yl)isophthalate (PIP), which has a lower symmetry in C_{2v} , compared to tricarboxylate ligands, but is still able to connect metal ions in three directions. We successfully obtained a discrete J_{17} -type Johnson hexadecahedron, denoted as **CIAC-115**, by linking the PIP ligands with the Ni_4 -TC4A units (Scheme 1). To the best of our knowledge, this is the first example of metal–organic cage compounds belonging to a J_{17} solid. Unexpectedly, the isostructural cobalt analogue of **CIAC-115** could not be achieved under the same reaction conditions. Instead, a bamboo stick-like one-dimensional (1D) coordination polymer, denoted as **CIAC-116**, was obtained.

CIAC-115 was synthesized and crystallized by a one-pot solvothermal reaction in dimethylformamide (DMF):methanol solutions containing *p*-*tert*-butylthiacalix[4]arene (H_4 TC4A), $NiCl_2 \cdot 6H_2O$, and 5-(pyridin-4-yl)isophthalic acid (H_2 PIP), affording green diamond-shaped crystals. Single-crystal X-ray diffraction revealed that **CIAC-115** crystals adopt the monoclinic

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Scheme 1. Illustration of the Assembly of $\{\text{Ni}_{40}\}$ Hexadecahedral Nanocage^a



^aThe yellow polyhedron denotes the arrangement of shuttlecock-like Ni_4 -TC4A SBUs.

$P2/n$ symmetry with cell parameters of $a = 36.664(7)$ Å, $b = 34.101(6)$ Å, $c = 46.617(8)$ Å, $\beta = 92.414(2)^\circ$, and $V = 58231(18)$ Å³. The structure of **CIAC-115** contains 10 shuttlecock-like Ni_4 -TC4A units and 16 bridging PIP ligands, featured as a nanometer-sized coordination cage. If each tetranuclear Ni_4 -TC4A cluster is viewed as a vertex and each PIP ligand as a triangular tile, the nanocage can be simplified as a hexadecahedron with a gyroelongated square bipyramidal geometry, that is, one of the Johnson solids, J_{17} . It is constructed by pillaring two square pyramids with a square antiprism (Figure 1). The J_{17} hexadecahedron can be described as $[3^{16}]$ in a face

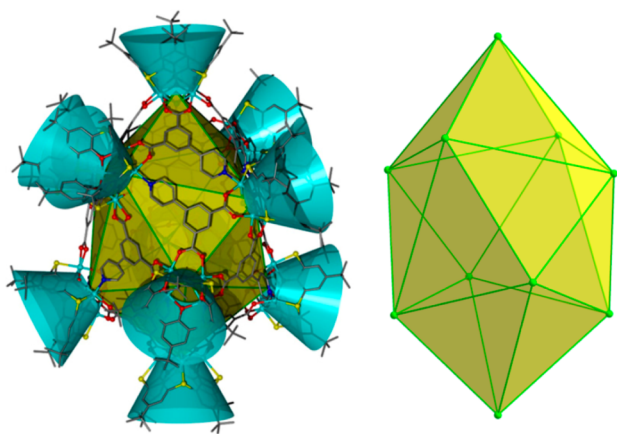


Figure 1. A discrete $\{\text{Ni}_{40}\}$ coordination cage of **CIAC-115** (left) and a schematic representation of the J_{17} Johnson-type solid (right) of $\{\text{Ni}_{40}\}$. The cyan truncated cones denote Ni_4 -TC4A SBUs and the yellow polyhedron represents their assembly.

symbol, denoting 16 three-membered rings, or $(3^4)_2(3^5)_8$ in a vertex symbol, indicating that there are two vertices, in which four three-membered rings are joined together, and eight vertices, in which five three-membered rings are joined together.⁹ The difference of the coordination numbers of the vertices reflects the distinct coordination modes between nickel atoms and the PIP ligands, which may bridge via $-\text{OCO}-$ or by one of the oxygen atoms of the carboxyl groups. Alternatively binding may occur by the nitrogen atom of pyridine group of the PIP ligand or chelating by the carboxylate group. In short, **CIAC-115**

represents the first J_{17} Johnson solid discovered for metal-organic polyhedra and the single $\{\text{Ni}_{40}\}$ entity made of 10 tetranuclear clusters ranks as the highest nuclearity in metal-organic Ni clusters ever reported.

The hexadecahedral cage strongly deforms from the ideal D_{4d} symmetry for a J_{17} solid. A 2-fold axis goes through the $\{\text{Ni}_{40}\}$ cage (Figure S2). Each asymmetric unit of the cage is composed of five Ni_4 -TC4A units, simplified as a square pyramid. The top view of the square pyramid (Figure 2) clearly shows the strong

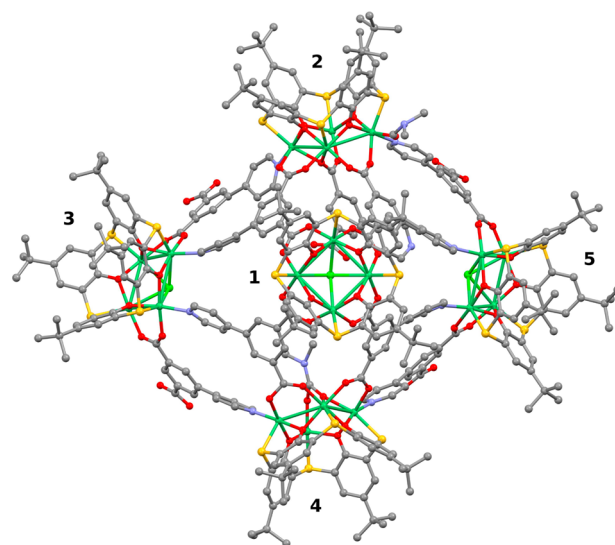


Figure 2. Asymmetric unit of the **CIAC-115** structure. C, gray; O, red; N, blue; S, yellow; Ni, green; Cl, lighter green. Hydrogen atoms and disordered groups are omitted for clarity. Five Ni_4 -TC4A clusters are marked with numbers.

distortion at the base of the pyramid. In each of the five tetranuclear Ni_4 -TC4A units, every phenoxo oxygen atoms bridge two nickel ions and four sulfur atoms coordinate four nickel atoms, respectively, as in our previously reported octahedral Co-TC4A cages.^{8b} In clusters 1, 3, and 5 (Figures 2 and S3), four nickel atoms are capped by a chlorine ion, resulting in a $\text{Ni}_4(\mu_4\text{-Cl})$ square pyramid. Whereas, nickel atoms are capped by disordered HCOO and PIP groups in cluster 2 and disordered CO_3 and Me_2NCOO groups in cluster 4, revealed by structure refinement. Since the starting materials do not contain HCOO, CO_3 , and Me_2NCOO , it is assumed that they were produced from the decomposition and oxidization of DMF. All four nickel atoms in cluster 1 have the same coordination modes toward the PIP ligands (Figure S3, 1a and 1b), as in the octahedral Co-TC4A cages,^{8b} in which each pair of adjacent metal atoms are bridged by an $-\text{OCO}-$ group of the PIP ligand. Therefore, each nickel atom is surrounded by two oxygen atoms in TC4A, one chlorine ion, one sulfur atom in TC4A, and two oxygen atoms from two adjacent PIP ligands. Clusters 3 and 5 have the same coordinate modes around the nickel atoms (Figure S3, 3a and 5a). At their lower rims, three $-\text{OCO}-$ groups bridge four nickel atoms and each pyridine in the two PIP ligands coordinates to a nickel atom, fulfilling the octahedral coordination geometry of each nickel atom. Clusters 2 and 4 have similar coordination modes, in which there are five PIP ligands coordinated to four nickel atoms (Figure S3, 2a and 4a). Among them, two $-\text{OCO}-$ groups bridge three nickel atoms, two pyridines coordinate to two nickel atoms separately, and one carboxylate group of the PIP ligand chelates a nickel atom. Aside

from different capping groups between clusters **2** and **4**, there is an extra DMF bound to a nickel atom in cluster **2** (Figure S3, **2a** and **2b**). Overall, the square pyramid is asymmetric, and each cage comprises two pyramids via a two-fold chiral axis. Therefore, the **CIAC-115** crystal is a racemic crystal that contains both left- and right-handed cage molecules.

The dimensions of the nanocage are approximately $40.5 \times 36.8 \times 31.7 \text{ \AA}^3$ measured from the opposite $C_{\text{butyl}} \cdots C_{\text{butyl}}$ of the structure, which is consistent to the result from the dynamic light scattering studies in solution (4.8 nm, Figure S9). The size of the inner cavity of the cage is about $23.8 \times 18.8 \times 13.9 \text{ \AA}^3$ measured between opposite HCOO^- and CO_3^{2-} groups and between the Cl atoms. The accessible volume of the compound for solvent and counter cations is 31629 \AA^3 per cell, as estimated by PLATON,¹⁰ which corresponds to 54.3% of the total crystal volume. The inner spaces inside the cage and between the cages are occupied by the $(\text{CH}_3)_4\text{N}^+$ cations and solvent molecules. These species could not be located from the residual electron density maps during the structure refinement because they are highly disordered. Their intensity contributions were subtracted from the diffraction data by the program SQUEEZE (see SI for details). The SQUEEZE results reveal that the approximate formula of **CIAC-115** is $[(\text{CH}_3)_4\text{N}]_3 \{[\text{Ni}_4(\text{TC4A})]_{10}(\text{Cl})_6(\text{PIP})_{16}(\text{HPIP})_{0.775}(\text{HCOO})_{1.225}(\text{CO}_3)_{0.9868}(\text{Me}_2\text{NCOO})_{1.0132}(\text{DMF})_{0.93924}\} x\text{DMF}$ ($x \approx 150$).

Dai and Wang reported two pairs of isostructural Co and Ni octahedral cages.^{7c} Anticipating the formation of the analogous $\{\text{Co}_{40}\}$ cage, we tried CoCl_2 instead of NiCl_2 under the same reaction conditions. Instead, a bamboo stick-like 1D coordination polymer, **CIAC-116**, was obtained. **CIAC-116** crystallizes in the tetragonal space group $P4/mnc$ (no. 128) with cell parameters of $a = b = 30.4471(19) \text{ \AA}$, $c = 21.8623(14) \text{ \AA}$, and $V = 20267(3) \text{ \AA}^3$. According to the SQUEEZE results **CIAC-116** has an appropriate chemical formula of $[(\text{CH}_3)_4\text{N}]_2 \{[\text{Co}_4(\text{TC4A})_4\text{Cl}_4[\text{Co}_4\text{Cl}_2(\text{OH})_4](\text{PIP})_8\} x\text{DMF}$ ($x \approx 22$). In contrast to **CIAC-115**, **CIAC-116** has only one type of coordination mode around the shuttlecock-like Co-TC4A units, i.e., the one in cluster **1** of **CIAC-115**. Four Co-TC4A units in a square arrangement are bridged by eight PIP ligand, four on each side of the square, providing a propeller-like SBU. The $\{(\text{Co}-\text{TC4A})_4(\text{PIP})_8\}$ SBUs are linked by a rare $\{\text{Co}_4(\mu_2\text{-O})_4(\mu_4\text{-Cl})_2\}$ cluster¹¹ and form a 1D chain resembling a bamboo stick (Figures 3 and S4). If $\text{Co}_4\text{-TC4A}$ and $\{\text{Co}_4\text{O}_4\text{Cl}_2\}$ units are viewed as vertices and PIP ligands as titles, the $\{(\text{Co}_4\text{-TC4A})_4(\text{Co}_4\text{O}_4\text{Cl}_2)_2(\text{PIP})_8\}$ entity is an elongated octahedral cage. Cages are connected at vertices, thus forming a chain polymer (Figure S4). As the effective ionic radii for six-coordinated Co^{2+} (high spin, 0.745 \AA) and Ni^{2+} (0.69 \AA) are small,¹² we anticipated that a $J_{17} \{\text{Co}_{40}\}$ cage could exist and

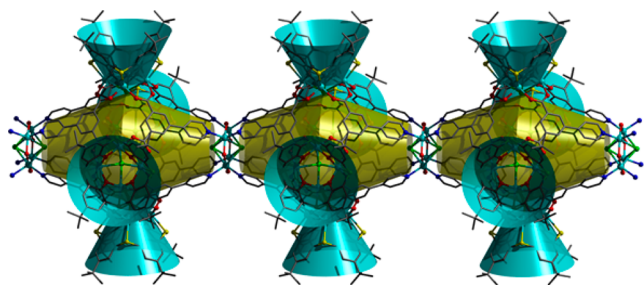


Figure 3. A section of 1D bamboo stick-like coordination assembly in **CIAC-116**. Yellow polyhedra depict the inner cavities.

would have marginal differences compared to its Ni analogue **CIAC-115** in terms of geometric parameters, including bond lengths and angles. Obviously two structure forms, cage-like vs 1D chain-like, compete during the assembling process, and the subtlety of exchanging Co for Ni is sufficient to impact the outcome.

Thermal analysis revealed that the **CIAC-115** crystals lost solvent in the crystal lattice between room temperature and $180 \text{ }^\circ\text{C}$ and that the desolvated sample remained stable up to $376 \text{ }^\circ\text{C}$ (Figure S10). We therefore concluded that the accessible space inside the **CIAC-115** cage may accommodate gas molecules. To prove the permanent porosity of the **CIAC-115** cage, gas adsorption measurements were carried out for the samples after exchanging the solvent and then activating at $100 \text{ }^\circ\text{C}$ under reduced pressure for 10 h. The N_2 sorption isotherm at 77 K reveals type-I adsorption behavior, indicating a microporous material with Brunauer–Emmett–Teller and Langmuir surface areas of 646 and $885 \text{ m}^2 \cdot \text{g}^{-1}$, respectively (Figure S13). Hysteresis is observed at the low-temperature isotherms of **CIAC-115** (e.g., N_2 and H_2 isotherms at 77 K , Figures S13–S14), which is presumably caused by the extrinsic porosity, i.e., free space between cages. A similar phenomenon was seen in a cage-like compound **MOSC-1-Ni**.^{7c} We also examined other gases. At the pressure of 1 bar, the adsorption capacity on CO_2 is $32.7 \text{ cm}^3 \cdot \text{g}^{-1}$ ($6.4 \text{ wt } \%$) at 298 K and $59.7 \text{ cm}^3 \cdot \text{g}^{-1}$ ($11.7 \text{ wt } \%$) at 273 K (Figure S15). The calculated isosteric heat (Q_{st}) of adsorption at zero CO_2 loading is $25.8 \text{ kJ} \cdot \text{mol}^{-1}$. The CH_4 uptake of **CIAC-115** at ambient pressure is $19.9 \text{ cm}^3 \cdot \text{g}^{-1}$ at 273 K and $12.5 \text{ cm}^3 \cdot \text{g}^{-1}$ at 298 K (Figure S16), and Q_{st} for CH_4 is $22.2 \text{ kJ} \cdot \text{mol}^{-1}$. The corresponding values for C_2H_6 and C_3H_8 are $31.8 \text{ cm}^3 \cdot \text{g}^{-1}$ at 273 K , $22.5 \text{ cm}^3 \cdot \text{g}^{-1}$ at 298 K , $35.4 \text{ kJ} \cdot \text{mol}^{-1}$ and $81.9 \text{ cm}^3 \cdot \text{g}^{-1}$ at 273 K , $59.7 \text{ cm}^3 \cdot \text{g}^{-1}$ at 298 K and $39.8 \text{ kJ} \cdot \text{mol}^{-1}$ (Figures S17–S19). **CIAC-115** exhibits much higher adsorption capacities on C_2H_6 and C_3H_8 compared to CH_4 , suggesting that **CIAC-115** can be used for the separation of these gases.

To simulate the separation behavior of **CIAC-115**, the gas selectivity of the binary mixtures CO_2/CH_4 , $\text{C}_2\text{H}_6/\text{CH}_4$, and $\text{C}_3\text{H}_8/\text{CH}_4$ was calculated via IAST based on the experimental single component isotherms fitted by the dual site Langmuir model at 298 K and 1 bar.^{13,14} The selectivities of CO_2/CH_4 at ratios of 50%/50% and 5%/95% were 3.0 and 0.15, respectively. The selectivities of $\text{C}_2\text{H}_6/\text{CH}_4$ and $\text{C}_3\text{H}_8/\text{CH}_4$ at a ratio of 50%/50% were 8.3 and 124.8, respectively (Figure 4), and these values (15.9 and 264.1) are almost doubled at 273 K (Figure S20). Notably the adsorption selectivity of C_3H_8 over CH_4 in **CIAC-115** is comparable with many examples reported. For example, its selectivity at 0.1 bar and 298 K is much better than the compound **FIR-7a-ht**¹⁵ and close to **UTSA-35a**,¹⁶ which makes it a good candidate for separating C_3H_8 and CH_4 .

In summary, we present a calixarene-based Johnson-type (J_{17}) coordination polyhedron **CIAC-115**, constructed by 10 shuttlecock-like $\text{Ni}_4\text{-TC4A}$ SBUs and 16 triangular PIP linkers and a 1D bamboo stick-like coordination polymer **CIAC-116**, assembled by linking octahedral $(\text{Co}_4\text{-TC4A})_4(\text{PIP})_8$ cages with octahedral $\{\text{Co}_4(\mu_2\text{-O})_4(\mu_4\text{-Cl})_2\}$ clusters. **CIAC-115** was synthesized based on the idea that linkers with low symmetry favor the creation of nonclassical polyhedra, such as Johnson solids. **CIAC-115** represents the first J_{17} -type hexadecahedral coordination cage and also features the highest nuclearity of $\{\text{Ni}_{40}\}$ among known Ni clusters. In addition, the activated sample of **CIAC-115** appears efficacious for the separation of C_3H_8 and CH_4 gases. Its successful preparation inspires us to search for and design a variety of asymmetric ligands for building other Johnson

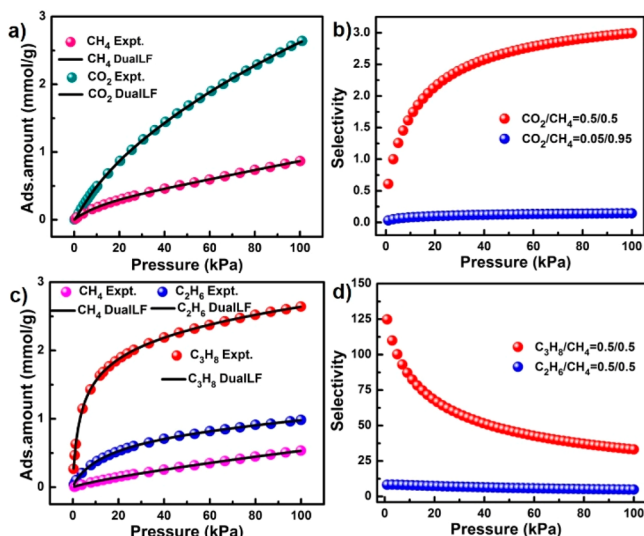


Figure 4. CO_2 , CH_4 , C_2H_6 , and C_3H_8 adsorption isotherms at 298 K along with the dual-site Langmuir Freundlich fits (a, c). Gas mixture adsorption selectivity is predicted by IAST at 298 K and up to 100 kPa for CIAC-115 (b, d).

solids. Our efforts to prepare these elegant calixarene-based molecular assemblies are ongoing.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00695.

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Notes

The authors declare no competing financial interest.

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(11) The search in the Cambridge Structural Database (version 2015) gave no hit on a $\{\text{M}_4(\mu_2\text{-O})_4(\mu_4\text{-Cl})_2\}$ cluster (M is any metal). If replacing Cl with any atom, only one relevant hit with a Refcode of DOYFED was found, which is a $\{\text{Cu}_4(\mu_2\text{-O})_4(\mu_4\text{-N})_2\}$ cluster.

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