A New Class of Cyclic Hexamer: $[Co_6L_6]^{24-}$ (H_6L = hexaazatriphenylene hexacarboxylic acid)

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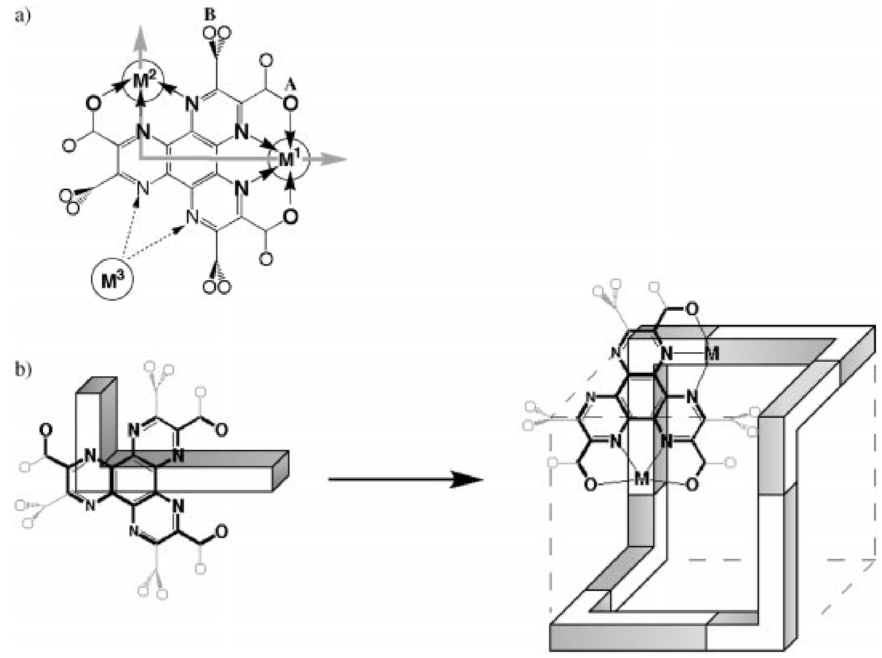

Figure 1. a) Coordination mode of L^{6-}. b) Schematic representation of the design and self-assembly of a cyclic nanostructure.

The design and construction of nano-sized polynuclear metal complexes with cyclic topologies are of great current interest as a result of their potential applications, such as molecular inclusion,[1, 2] as well as their electrochemical,[3] magnetic,[4] and/or photophysical properties.[5] Of particular interest are molecular modules containing multifunctional ligands with π-electronic structures which could provide unique electronic properties. Hexaazatriphenylene (hat) and its derivatives, which are multifunctional ligands with π-electronic structures, have been studied in the fields of supramolecular chemistry, photochemistry, and crystal engineering.[1, 6] Recently we have synthesized a trinuclear copper(I) complex containing the stable radical anion $[hat(CN)_6]^{\bullet -}$ which indicates that the peripheral substituents influence the electronic structure, in particular, the low-lying π* orbitals of the hat moiety.[7] Herein we report the synthesis of a novel cyclic molecular module containing a hat derivative which indicates that the peripheral substituents can control not only the electronic structure but also its coordination modes.

The key feature of this successful synthesis is the design of a hat derivative whose coordination topology is controlled by carboxylate groups, in this case hexaazatriphenylene hexacarboxylic acid (H_6L). L^{6-}, the deprotonated form of H_6L, functions as a quadridentate chelate ligand (two aromatic nitrogen atoms and two carboxylate oxygen atoms). The carboxylate groups involved in the chelate coordination (A in Figure 1 a) lie on the same plane of the aromatic moiety of the L^{6-} unit. The nearest-neighbor carboxylate group (B in Figure 1 a) sits perpendicularly to the plane because of the steric hindrance. Therefore, each carboxylate group is arranged in an ABABBA fashion. In this way the three donor atoms participate in the coordination of a second metal cation, to form a tridentate chelate coordination. The coordination of the two metal cations cause a marked decrease in the basicity of the other remaining nitrogen donors, which could be a principal reason for the coordination of no further cobalt cations. Consequently L^{6-} acts as a building block with a right angle, which is useful for constructing a cyclic nanostructure[8] (Figure 1 b). The spontaneous assembly of these subunits is shown schematically in Figure 1 b. Since L^{6-} acts as a building block with a right angle and the metal center links two L^{6-} ligands perpendicularly, the formation of the unique nano-sized cyclic hexamer is expected through a molecular self-assemble process. In the resulting cyclic structure six out of the eight corners of a cube are connected (Figure 1 b).

The reaction of $Co(NO_3)_2 \cdot 6\,H_2O$ with Na_6L in acetonitrile/H_2O results in the novel cyclic hexamer $\{[Co(H_2O)_6]_{10}[Co_6\{Co(H_2O)_3\}_2\{\mu_3\text{-}L\}_6]\cdot 74\,H_2O\}_n$ (**1**), which was characterized by X-ray crystallography. The structure of **1** has four unique features:

1. distorted pentagonal-bipyramidal cobalt(II) centers,
2. nano-sized (ca. 2 nm) cyclic units,
3. a cobalt complex encapsulated in the central cavity of the cyclic unit,
4. a two-dimensional honeycomb layer.

As regards point 1, the coordination geometry around the Co center which constructs the cyclic units is shown in Figure 2. The four aromatic nitrogen atoms and three carboxylic oxygen atoms form a distorted pentagonal bipyramid around the Co^{II} center; the N(3) and O(5) atoms are in the axial positions and the N(3)-Co-O(5) angle is 152.7(3)°. Two oxygen atoms, O(1) and O(3), coordinate weakly (Co–O(1): 2.458(8), Co–O(3): 2.347(7) Å) compared with the others (bond lengths: Co–O(5): 2.138(7), Co–N(1): 2.151(8), Co–N(2): 2.120(7), Co–N(3): 2.281(7), and Co–N(4): 2.030(8) Å). There have been to date several examples of seven-coordinate pentagonal-bipyramidal cobalt(II) complexes which have the equatorial plane made up of the five coordination atoms of a quinquedentate ligand,[9] except for examples of nitrate anions functioning as chelate

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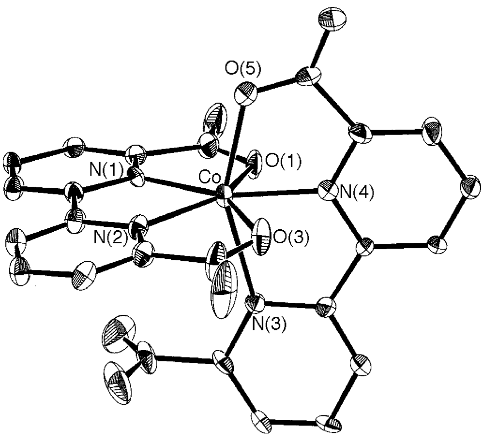

Figure 2. Coordination geometry around the Co center that constructs the cyclic unit.

ligands.[10] To the best of our knowledge, the complex reported here is the first example of a seven-coordinate pentagonal-bipyramidal cobalt(II) complex comprised of quadridentate and tridentate ligands.

The structure of the nano-sized cyclic hexamer (see point 2) formed by six Co^{II} ions and six L^{6-} ligands is illustrated in Figures 3 and 4. Figure 3 highlights the cyclic framework, which is consistent with our design shown in Figure 1 b. The cyclic module (Figure 4) has an S_6-symmetrical screwlike structure. The distance between the opposite cobalt atoms of the unit is 13.68 Å. When the van der Waals radii are taken into consideration, the diameter of the ring is about 2 nm and that of the cavity is approximately 1 nm.

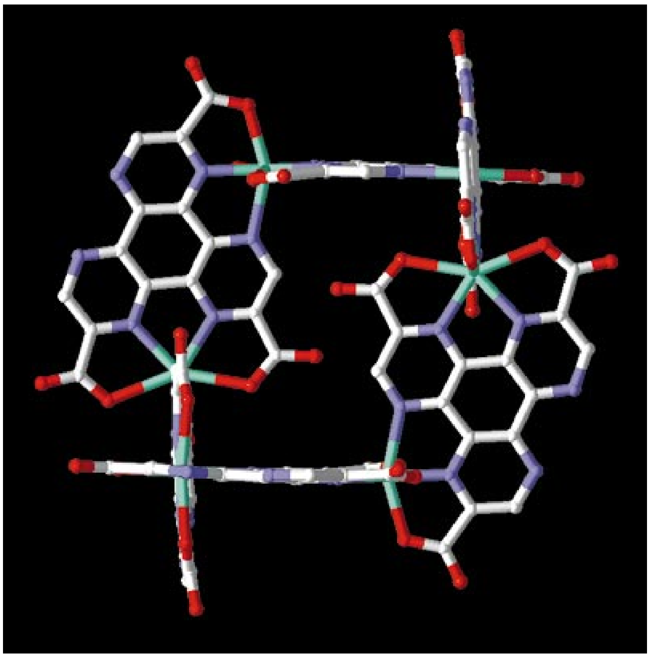

Figure 3. Structure of the cyclic hexamer in the solid state. Carboxylate groups which do not join in the formation of the cycle are omitted for clarity. Color code: C: white, N: blue, O, red, Co: green.

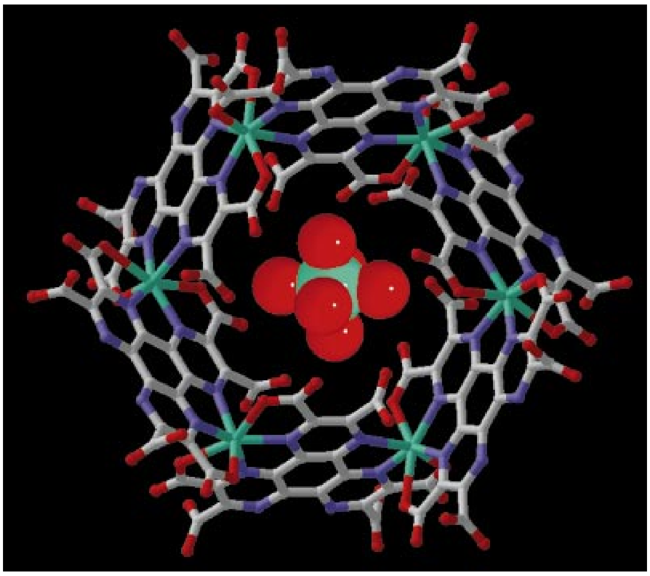

Figure 4. Structure of the cyclic module along the *c* axis. A hexaaquacobalt(II) cation is encapsulated in the central cavity of the cyclic module.

In the construction of cyclic nanostructures (point 3) it is very important to control not only the angles of the subunits but also the templating effect. In the case of **1**, a hexaaquacobalt(II) cation ($[Co(H_2O)_6]^{2+}$) is encapsulated in the central cavity of the cyclic hexamer. The water molecules of the guest complex are hydrogen-bonded to carboxylate groups from the cyclic hexamer, and acts in a supporting role for the formation of the cyclic framework.

The three residual carboxylate groups which do not participate in the formation of the cycle are involved in the module-link framework (see point 4). One of them acts as the secondary interaction site to link the cyclic units. The coordination of the carboxylate groups to another cobalt(II) ion leads to a facial-type coordination geometry with the six oxygen atoms (three from the water molecules and three from the carboxylate groups) to form a two-dimensional honeycomb layer in the *ab* plane (Figure 5). The L^{6-} ligand has three different coordination sites: quadridentate and tridentate chelate coordination sites to form the cyclic unit and a monodentate coordination site to form the honeycomb layer.

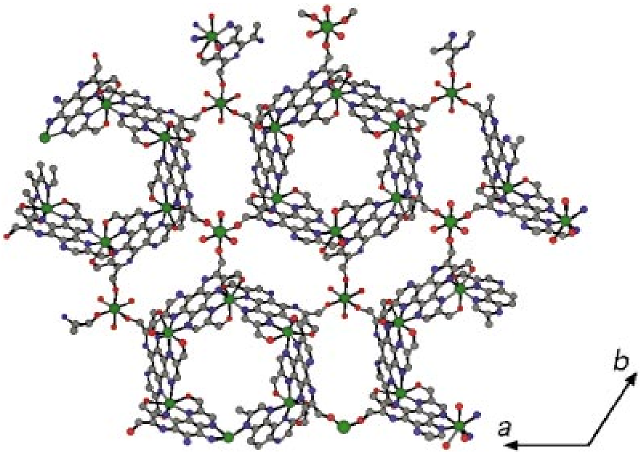

Figure 5. Honeycomb layer structure of **1** in the *ab* plane.

The crystal structure of **1** shows there are three hexaaquacobalt(II) complexes per cyclic unit that are located between the cyclic units in the honeycomb layer and act as countercations, and a further six complexes that are located between the honeycomb layers. The anionic honeycomb layers and the cationic layers composed of hexaaquacobalt(II) cations lie alternately along the *c* axis and results in a canceling out of their electrical charge.

The electronic absorption spectrum of **1** in the solid state has an intense band centered at 383 nm, which is dissimilar to that of the ligand alone with two π-π* transition bands centered at 293 and 336 nm, and is therefore attributed to the metal-to-ligand charge-transfer transition in the cyclic core. The magnetic susceptibilities of **1** over the temperature range 2–300 K show a monotonous decrease in the $\chi_m T$ value (from 7.07 emu K mol^{-1} at room temperature) with decreasing temperature.

In this work we have succeeded in the design and synthesis of a novel cyclic module with a hexacarboxylate derivative. These results have important implications for the design of nano-scaled materials.

Experimental Section

1: H_6L (prepared from a literature procedure[11]) was added to an aqueous NaOH solution. An acetonitrile solution of $Co(NO_3)_2 \cdot 6H_2O$ was carefully layered on top of the aqueous solution and the mixture allowed to stand for one month. The red prismatic crystals obtained were collected by filtration (65% yield). Elemental analysis calcd for $C_{18}H_{22}Co_3N_6O_{23} \cdot 4H_2O$: C 23.02, H 3.22, N 8.95; found: C 22.70, H 2.80, N, 9.27.

X-ray structure determination of **1**: All data were measured on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. The structure was solved by Patterson methods (DIRDIF92 PATTY). The water molecules of the $[Co(H_2O)_6]^{2+}$ ion encapsulated in the central cavity of the cyclic hexamer were disordered, and were modeled as oxygen atoms with 33.33% occupancy factors. Non-hydrogen atoms which were not disordered were refined anisotropically, except for the solvent water molecules. All the water molecules were modeled as oxygen atoms. Refinement was carried out with full-matrix least-squares on F^2. All calculations were performed with the TEXSAN crystallographic software package. Crystal data for $C_{18}H_{22}Co_3N_6O_{23} \cdot 12.33H_2O$: $M_r = 1089.34$, crystal size $0.20 \times 0.20 \times 0.20$ mm, trigonal, space group $R\bar{3}$ (No. 148), $a = 22.632(3)$, $c = 39.794(3)$ Å, $V = 17652(3)$ Å^3, $Z = 18$, $\rho_{calcd} = 1.844$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $F(000) = 10085.58$, $\mu(Mo_{K\alpha}) = 13.80$ cm^{-1}, $T = 25$ °C, $2\theta_{max} = 54.2°$. Of the 32745 reflections collected, 8580 were unique ($R_{int} = 0.043$). For 4373 reflections with $I > 4.00\sigma(I)$, 518 parameters; $R(R_w) = 0.087(0.238)$. Min./max. residual electron density $-0.88/1.10$ e$^-$ A^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161830. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Chaotropic Anions Strongly Stabilize Short, N-Capped Uncharged Peptide Helicies: A New Look at the Perchlorate Effect[**]

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In the course of an analysis of the pH-dependent helicity of short alanine peptides N-capped with helix-initiating templates of the Ac-Hel family,[1] we noted a remarkable helix stabilization caused by binding of anions with low hydration volumes, the so-called chaotropic anions.[2] These are well-known to bind both to pH-denatured proteins[3] and to helically disposed polycationic peptides,[4] electrostatically shielding and thereby stabilizing partially folded conformations such as helices. We now demonstrate efficient anion-induced helix stabilization for short N-capped polyalanines that lack charged groups. In addition to the helix-inducing N-cap these polyalanine peptides also contain recently reported N- or C-caps that solubilize the polyalanine se-

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