Inorg. Chem. **2008**, *47*, 8126−8133

Inorganic Chemistry
Article

Assembly of a Cubic Nanocage Co_8L_{12} and a Hydrogen-Bonded 3D NbO Net Based on the $[(HCO_3)_2]^{2-}$ Synthon and Water

Man-Li Cao, Hong-Guo Hao, Wei-Xiong Zhang, and Bao-Hui Ye*

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

Received April 2, 2008

Two new complexes $[Co(H_2O)_6{\subset}Co_8(L1)_{12}]X_6 \cdot nH_2O$ ($X = NO_3^-$, $n = 12$ (**1**); $X = HCO_3-$, $n = 24$, (**2**); HL1 = 4,6-bis(2-pyridyl)-1,3,5-triazin-2-ol) have been synthesized and characterized by single-crystal X-ray diffraction. A $[Co(H_2O)_6]^{2+}$ ion is encapsuled in the central cavity of the cubelike nanocage $[Co(H_2O)_6{\subset}Co_8(L1)_{12}]^{6+}$ cation, assembled by eight cobalt ions at the corners and twelve bis-bidentate ligands L1 as the edges, via the formation of 12-fold strong hydrogen bonds between the six coordinated water molecules and the oxygen atoms of twelve L1 as a guest. Complex **1** crystallizes in a centrosymmetric space group $P\bar{1}$, while **2** is in a very high symmetric space group $Im\bar{3}$. In **2**, a planar $[(HCO_3)_2]^{2-}$ dimer motif $R_2^2(8)$ synthon plus six lattice water molecules constitute a planar supramolecular synthon $R_8^8(20)$, which acts as a four connector, generating a 3D hydrogen-bonded NbO net with cubelike host cavities of ∼20 Å diameter. Interestingly, the cubelike nanocage $[Co(H_2O)_6{\subset}Co_8(L1)_{12}]^{6+}$ cations fill in the cavities as templates. The magnetic properties of **1** have also been studied in the temperature range of 2−300 K, and its magnetic susceptibility obeys the Curie−Weiss law, showing antiferromagnetic coupling.

Introduction

The cagelike molecules,[1−4] presenting both challenges and opportunities for synthetic chemists because of their utility as possible drug delivery agents,[5] reaction nanocontainers and catalysts,[6] storage materials,[7] and environments within which to protect and study reactive intermediates,[8] have grown rapidly. With respect to synthesis, there is a great deal of interest in metal-induced self-assembled supramolecular cages using the ability of coordination bond to direct orientation of the desired components.[3,6c,9] Two approaches have been used to assemble into the cubic cage. The first is edge-directed self-assembly of the linear components linked at the corner. In this case, eight tritopic units with 90° angles, together with twelve linear ditopic linkers, are required to generate six closed circuits each containing four nodes. Following this strategy, several M_8L_{12} and $M_{12}L_8$ instances have been exploited.[10,11] The second is face-directed self-assembly of the facial components linked either at the edges or at the corners. Three examples M_4L_2, M_6L_8, and M_6L_{12} constructed via such approach have been reported.[12−14] Although the template assembly has been suggested to be an effective approach for the construction of the cagelike supramolecules,[15] only two cubelike instances have been reported based on the alkali metal ions or anions as templates.[10d,f]

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* To whom correspondence should be addressed. Fax: (86)-20-84112245. Phone: (86)-20-84112469. E-mail: cesybh@mail.sysu.edu.cn.

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10.1021/ic800585d CCC: $40.75

To obtain cagelike structural motifs, a large number of bis-bidentate ligands have been designed and synthesized. In this context, it has been well documented that the bis-bidentate ligands can bind to metal ions to yield a 1D chain (ML), dinuclear or double helices (M_2L_2), triple helices (M_2L_3), triangle (M_3L_3), [2 × 2] grid (M_4L_4), tetrahedron (M_4L_6), pentagon (M_5L_5), and hexagon (M_6L_6, see Scheme 1) depending on the ratio of metal ion toward ligand, the coordination number of metal ions, template reagent, and so on.[16] We are aware of only one instance of X-ray structural elucidations of a cubelike complex constructed by a self-assembly of eight zinc ions and twelve flexible, bis-bidentate ligands in the presence of anion (BF_4^- or ClO_4^-), in which the zinc ion locates at the corner and the 2,6-bis(3-(pyrid-2-yl)pyrzol-1-ylmethyl)-pyridine ligand as the edge.[10f] Among the diversiform, rigid bis-bidentate ligands, the N,N-chelating oligopyridine ligands, especially those containing the pyrimidine or triazine ring as a bridge, have much attracted our attention. In fact, three kinds of such ligands L2−L4 (see Scheme 2,) have been assembled with metal ions and characterized by single crystal X-ray diffraction. Only the mononuclear,[17] binuclear,[18] [2 × 2] grid,[19] and 1D chain[18b] motifs were constructed in the mild conditions, to the best of our knowledge. The ligand 4,6-bis(2-pyridyl)-1,3,5-triazin-2-ol (HL1) has six potential coordinate sites; it may offer a bis-bidentate binding mode with the capability of bridging two metal ions in chelating manner. In the present case, the OH group can deprotonate and further coordinate to metal ions or form hydrogen bonding with the donated groups. Although the HL1 was synthesized in 2005,[20] the coordination chemistry of this multitopic ligand has not yet been explored. We hope that the HL1 ligand could possibly generate new architectures that would exploit the new motifs of this kind of ligand. We report herein the synthesis, structural characterization, and magnetic properties of the new complex $[Co(H_2O)_6\subset Co_8(L1)_{12}](NO_3)_6\cdot 12H_2O$ (**1**), in which L1 is a bis-bidentate ligand at the edge, the cobalt(II) ion locates at the corner of the cube, and a $[Co(H_2O)_6]^{2+}$ ion embeds in the central cavity as a guest, which plays an indispensable role in the cage structure formation. Furthermore, when **1** is dissolved in an aqueous solution of K_2CO_3 or $KHCO_3$, complex $[Co(H_2O)_6\subset Co_8(L1)_{12}](HCO_3)_6\cdot 24H_2O$ (**2**) was obtained, in which the $[Co(H_2O)_6\subset Co_8(L1)_{12}]^{6+}$ cations as guests were encapsuled in a 3D hydrogen-bonded host framework based on the hydrogen carbonate dimer and water molecules.

Experimental Section

Materials and Methods. The reagents and solvents employed were commercially available and were used as received without further purification. The C, H, and N microanalyses were carried out with a Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 400−4000 cm^{-1} on a Bruker TENSOR 27 spectrometer. ^1H NMR spectra were recorded on a Varian 300 MHz spectrometer at 25 °C. Electron spray ionization (ESI) mass spectra were obtained on a LCQ DECA XP quadrupole ion trap mass spectrometer with methanol as the carrier solvent. Thermogravimetric data were collected on a Netzsch TGS-2 analyzer in nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Powder X-ray diffraction patterns were recorded on a D/Max-2200 diffractometer with Cu Kα radiation ($\lambda = 1.5409$ Å) at a scanning rate of 4° min^{-1} with 2θ ranging from 4° to 40°. The microcrystalline samples used for magnetic measurement were checked by powder X-ray diffraction to confirm the purity. Magnetic susceptibility data of powder samples were collected in the temperature range of 2−300 K in an applied field of 1000 Oe with the use of a Quantum Design MPMS7 SQUID magnetometer. The diamagnetic corrections were estimated from Pascal's constants.[21] The effective magnetic moment was calculated from the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

Synthesis of HL1. HL1 was prepared according to previously reported procedures.[20] Yield: 56%. ESI-MS: $m/z = 250$. FT-IR (KBr, cm^{-1}): 3755 (w), 3240 (s), 3064 (m), 2924 (m), 1686 (m), 1645 (m), 1582 (vs), 1545 (vs), 1487 (vs), 1431 (vs), 1379 (s), 1290 (w), 1257 (w), 1142 (w), 1028 (w), 1001 (m), 806 (s), 754 (s), 675 (s), 627 (s), 584 (s). ^1H NMR data (DMSO-d_6, ppm): 8.52 (d, $J = 3.91$ Hz, 2H), 8.41 (d, $J = 7.87$ Hz, 2H), 7.94 (t, 2H), 7.48 (t, 2H).

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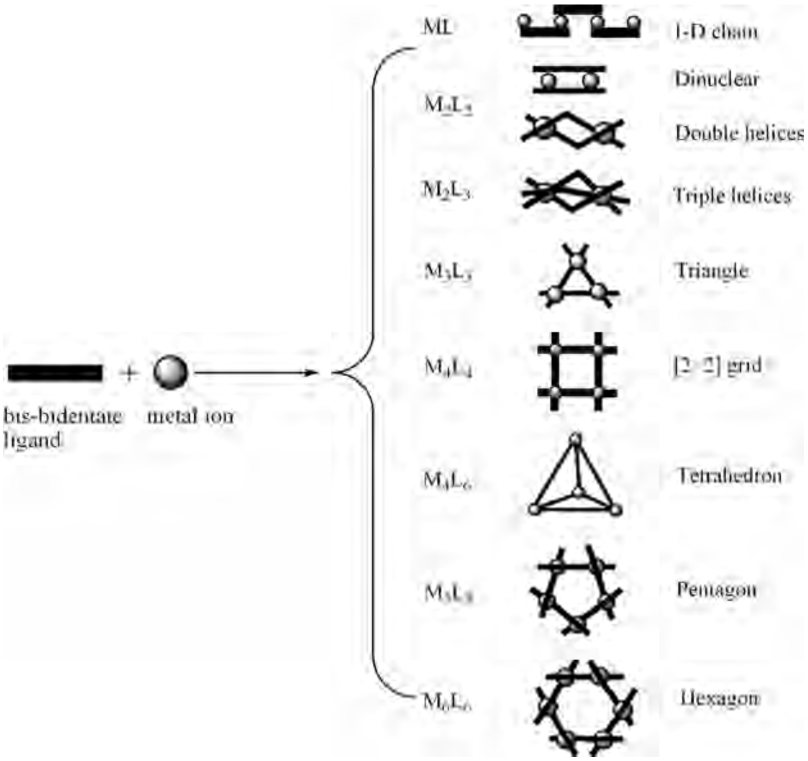
Scheme 1. Self-Assembly of Various Motifs from the Bis-bidenate Ligand and Metal Ions



Scheme 2. Molecular Structures of the Ligands

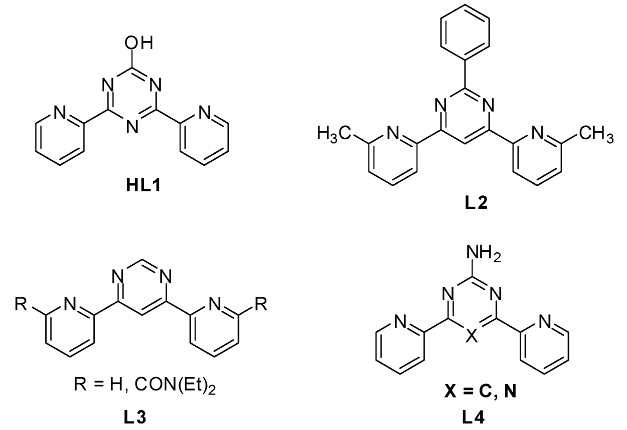


Table 1. Crystal Data and Structure Refinement for Complexes **1** and **2**

complex	1	2
molecular formula	$C_{156}H_{132}Co_9N_{66}O_{48}$	$C_{162}H_{168}Co_9N_{60}O_{60}$
fw	4229.65	4445.83
cryst syst	triclinic	cubic
space group	$P\bar{1}$	$Im\bar{3}$
a (Å)	17.922(2)	21.3615(9)
b (Å)	17.986(2)	21.3615(9)
c (Å)	18.080(2)	21.3615(9)
α (deg)	62.854(2)	90
β (deg)	60.600(2)	90
γ (deg)	88.026(2)	90
V (Å^3)	4381.2(8)	9747.5(7)
Z	1	2
ρ_{calcd} (g cm^{-3})	1.603	1.515
μ (mm^{-1})	0.932	0.845
reflns collected	19 834	9832
independent reflns	16 906	1729
data/restraints/params	9497/8/1248	1103/1/127
R indices [$I > 2\sigma(I)$], wR2 (all data)^a	0.0846, 0.2278	0.0644, 0.1993
GOF	1.012	1.007
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.72/−0.49	0.65/−0.62

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Synthesis of $[Co(H_2O)_6\subset Co_8(L1)_{12}](NO_3)_6\cdot 12H_2O$ (1). HL1 (0.125 g, 0.5 mmol), $Co(NO_3)_2\cdot 6H_2O$ (0.145 g, 0.5 mmol), 7 mL of distilled water, and 7 mL of ethanol were put into a 25 mL Teflon-lined Parr vessel. The mixture was heated to 120 °C for 72 h and then cooled to room temperature at a rate of 5 °C h^{-1}. The resulting solution was filtered, and the filtrate was kept in the dark at the room temperature. Red crystals were obtained after 1 week. Yield: 0.137 g, 78% (base on HL1). Anal. Calcd for $C_{156}H_{132}N_{66}O_{48}Co_9$ **1**: C, 44.26, H, 3.12, N, 21.84%. Found: C, 44.35, H, 3.32, N, 21.66%. FT-IR (KBr, cm^{-1}): 3300 (s), 1645 (s), 1545 (s), 1504 (vs), 1466 (vs), 1389 (vs), 1298 (w), 1265 (w), 1153 (w), 1022 (m), 800 (m), 758 (m), 714 (m), 677 (m), 642 (m), 584 (m).

Synthesis of $[Co(H_2O)_6\subset Co_8(L1)_{12}](HCO_3)_6\cdot 24H_2O$ (2). Compound **1** (0.084 g, 0.02 mmol) was added to 20 mL of 1 M K_2CO_3 or $KHCO_3$ aqueous solution to give an orange solution. The solution was slowly evaporated at room temperature, and red crystals were obtained after two weeks. Yield: 0.085 g, 95%. Anal. Calcd for $C_{162}H_{168}Co_9N_{60}O_{60}$ **2**: C, 43.76, H, 3.81, N, 18.90%. Found: C, 43.48, H, 3.89, N, 18.75%. FT-IR (KBr, cm^{-1}): 3306 (s), 1639 (vs), 1543 (s), 1506 (s), 1466 (s), 1392 (s), 1265 (w), 1148 (w), 1096 (w), 1022 (m), 802 (m), 758 (m), 712 (m), 677 (m), 636 (m), 580 (m).

X-ray Crystallography. Diffraction intensities for **1** and **2** were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS.[22] The structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXS-97 and SHELXL-97 pro-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1** and **2**[a]

	1		
Co1−N4	2.127(5)	Co1−N5	2.149(6)
Co1−N6	2.160(6)	Co1−N7	2.133(5)
Co1−N29	2.133(5)	Co1−N30	2.153(6)
Co2−N9	2.150(5)	Co2−N10	2.134(6)
Co2−N11	2.161(6)	Co2−N12	2.132(5)
Co2−N24A	2.120(6)	Co2−N25A	2.149(6)
Co3−N14	2.146(5)	Co3−N15	2.132(6)
Co3−N16	2.139(6)	Co3−N17	2.138(5)
Co3−N1A	2.159(6)	Co3−N2A	2.137(5)
Co4−N19	2.144(6)	Co4−N20	2.160(6)
Co4−N21	2.150(6)	Co4−N22	2.150(6)
Co4−N26	2.166(6)	Co4−N27	2.124(6)
Co5−O1W	2.058(5)	Co5−O2W	2.066(5)
Co5−O3W	2.068(5)		
N4−Co1−N7	103.3(2)	N4−Co1−N5	77.4(2)
N4−Co1−N29	104.1(2)	N4−Co1−N30	172.2(2)
N4−Co1−N6	83.0(2)	N5−Co1−N7	172.4(2)
N5−Co1−N6	95.5(2)	N5−Co1−N30	95.1(2)
N5−Co1−N29	83.1(2)	N6−Co1−N7	77.1(2)
N6−Co1−N29	172.3(2)	N6−Co1−N30	95.9(2)
N7−Co1−N30	83.9(2)	N7−Co1−N29	104.0(2)
N29−Co1−N30	76.7(2)	N9−Co2−N12	102.9(2)
N9−Co2−N10	76.3(2)	N9−Co2−N11	82.5(2)
N9−Co2−N24A	105.1(2)	N9−Co2−N25A	171.3(2)
N10−Co2−N11	95.3(2)	N10−Co2−N12	171.4(2)
N10−Co2−N24A	84.4(2)	N10−Co2−N25A	95.4(2)
N11−Co2−N12	76.2(2)	N11−Co2−N24A	172.0(2)
N11−Co2−N25A	95.9(2)	N12−Co2−N25A	85.0(2)
N12−Co2−N24A	104.0(2)	N24A−Co2-N25A	76.2(2)
N14−Co3−N15	76.6(2)	N14−Co3−N16	171.5(2)
N14−Co3−N17	104.0(2)	N14−Co3−N1A	82.1(2)
N14−Co3−N2A	103.0(2)	N15−Co3−N16	95.2(2)
N15−Co3−N17	84.7(2)	N15−Co3−N2A	171.0(2)
N15−Co3−N1A	94.8(2)	N16−Co3−N17	76.7(2)
N16−Co3−N1A	96.9(2)	N16−Co3−N2A	84.9(2)
N17−Co3−N2A	104.0(2)	N17−Co3−N1A	173.5(2)
N1A−Co3-N2A	76.43(2)	N19−Co4−N20	76.1(2)
N19−Co4−N21	171.4(2)	N19−Co4−N22	103.6(2)
N19−Co4−N27	103.5(2)	N19−Co4−N26	82.7(2)
N20−Co4−N21	95.4(2)	N20−Co4−N22	82.2(2)
N20−Co4−N26	95.7(2)	N20−Co4−N27	171.6(2)
N21−Co4−N22	76.1(2)	N21−Co4−N26	97.1(2)
N21−Co4−N27	84.6(2)	N22−Co4−N26	172.6(2)
N22−Co4−N27	105.9(2)	N26−Co4−N27	76.0(2)
O1W−Co5−O2W	90.3(2)	O1W−Co5−O3W	89.9(2)
O1W−Co5−O1WA	180.0(3)	O2W−Co5−O3W	90.3(2)
	2		
Co1−N1	2.164(4)	Co1−N2	2.138(4)
Co2−O1W	2.040(7)		
N2−Co1−N1A	83.4(1)	N2−Co1−N1	75.9(1)
N2−Co1−N2A	105.1(1)	N1−Co1−N1A	94.9(1)
N2−Co1−N1A	170.5(1)	O1WB−Co2-O1W	180.0
O1W−Co2−O1WA	90.0		

[a] Symmetry code for **1**: A, $-x + 1$, $-y + 1$, $-z + 1$. For **2**: A, z, x, y; B, $-x$, $-y$, $-z$.

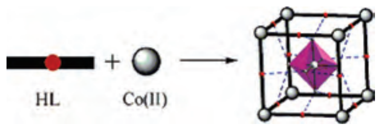
grams, respectively.[23,24] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C−H = 0.96 Å and N−H = 0.86 Å). The hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Crystal data, as well as details of data collection and refinement for the complexes, are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2, and the hydrogen bonding parameters are shown in Table 3.

Table 3. Hydrogen Bonding Parameters in **1** and **2**

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	∠D−H···A (deg)
		1		
O1W−H1WA···O1	0.84	1.86	2.692(7)	174.4
O1W−H1WB···O5A	0.82	1.88	2.659(7)	159.1
O2W−H2WB···O3	0.88	1.84	2.681(7)	158.8
O2W−H2WA···O6A	0.90	1.82	2.662(7)	155.8
O3W−H3WA···O4	0.83	1.89	2.676(7)	158.4
O3W−H3WB···O2	0.85	1.85	2.689(7)	168.3
		2		
O1W−H1WA···O1	0.83	1.86	2.691(6)	179.6
O2W−H2WA···O2	0.89	1.63	2.52(2)	180
O2W−H2WB···O3WA	0.85	1.87	2.71(1)	170.7
O3W−H3WA···O3	0.85	1.82	2.66(1)	170.5
O3W−H3WC···O2WB	0.92	1.94	2.71(1)	139
O3−H3B···O3C	0.86	1.75	2.61(1)	180

[a] Symmetry code for **1**: A, $-x + 1$, $-y + 1$, $-z + 1$. For **2**: A, $-y + 1/2$, $-z + 1/2$, $-x + 1/2$; B, $-z + 1/2$, $-x + 1/2$, $-y + 1/2$; C, $-x$, y, $-z + 1$.

Scheme 3. Diagram for the Formation of the Cubelike Structure



Results and Discussion

Synthesis and Characterization. The ligand HL1 was prepared by the reaction of 2-cyanopyridine and urea in the presence of sodium hydride as a catalyst in DMSO solution according to the previous report.[20] It is soluble in common organic solvents, such as MeOH, CH_3CN, DMF. In general, HL1 is a potential multitopic ligand with different coordination modes, such as tridentate terpyridine-like, bidentate bipyridine-like, and tetradentate bis-bipyridine-like.[25] Indeed, reaction of $Co(NO_3)_2 \cdot 6H_2O$ with HL1 in a 1:1 ratio in a water−ethanol mixture solution under solvothermal conditions afforded **1**. The structure reveals **1** to be a cubelike stucture with the metal ions at the corners and the bridging ligands L1 along the edges, in which the ligand is deprotonated and acts as tetradentate bis-bipyridine-like unit bridging two Co(II) ions via the triazine ring in chelating manner. A $[Co(H_2O)_6]^{2+}$ ion is encapsuled in the central cavity of the cube with very strong hydrogen bonding between the coordinated water molecules and the oxygen atoms of L1 as a guest. Survey of the CSD[26] for the analogous ligands with two pyridine arms connected to a pyrimidine or triazine spacer revealed that only the mononuclear,[17] binuclear,[18] [2 × 2] grid,[19] and 1D chain[18b] motifs were constructed. In the present case, the formation of cubic structure may be related to the strong hydrogen-bonded interaction between the deprotonated OH group and the $[Co(H_2O)_6]^{2+}$ ion. The six coordinated water molecules may donate 12-fold hydrogen bonds to the OH groups from 12 L1 (or HL1)

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(26) *Cambridge Structural Database*, version 5.28; CCDC: Cambridge, U.K., 2007.

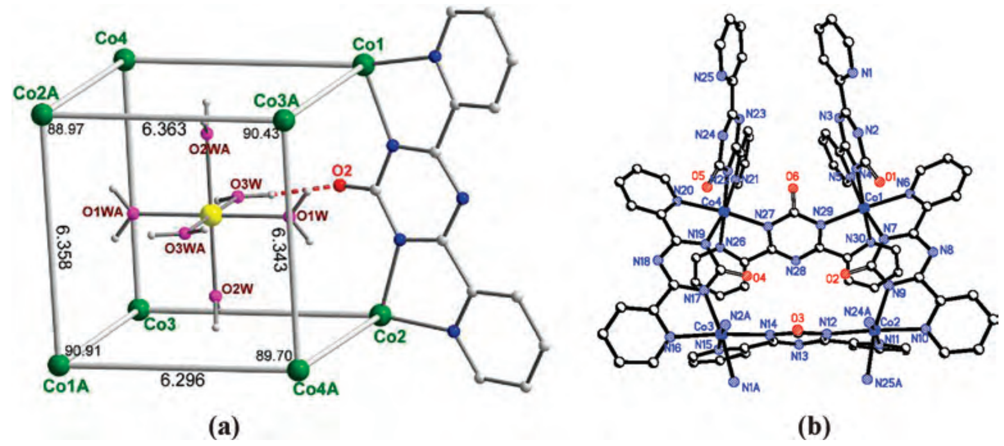

Figure 1. (a) View of the cationic structure of **1** with only one bridging ligand shown for clarity. (b) Asymmetric unit of the cube with part atoms omitted, each Co(II) has a *fac* arrangement. Symmetry code: A 1 − *x*, 1 − *y*, 1 − *z*.

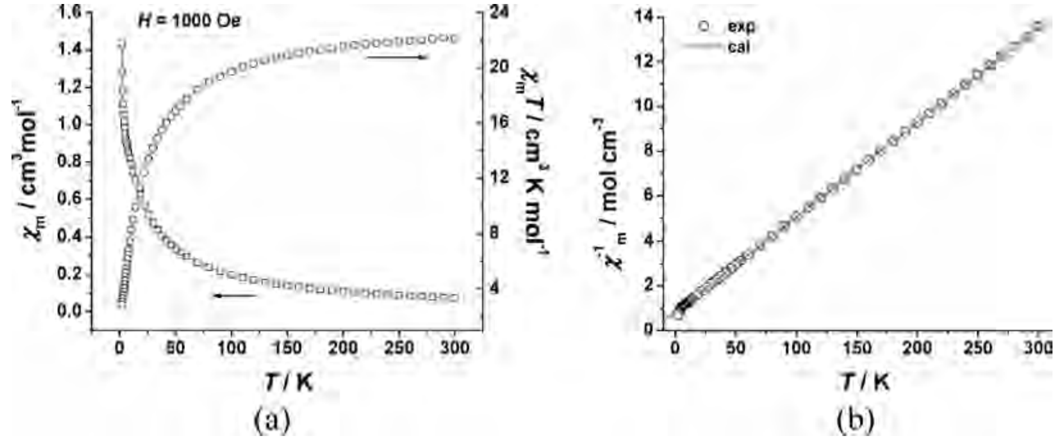

Figure 2. (a) Temperature dependence of magnetic properties of compound **1** in the form of $\chi_M T$ vs T (○) and χ_M vs T (□). (b) The plot of $1/\chi_M$ vs T. The solid line is the fitting of experimental data.

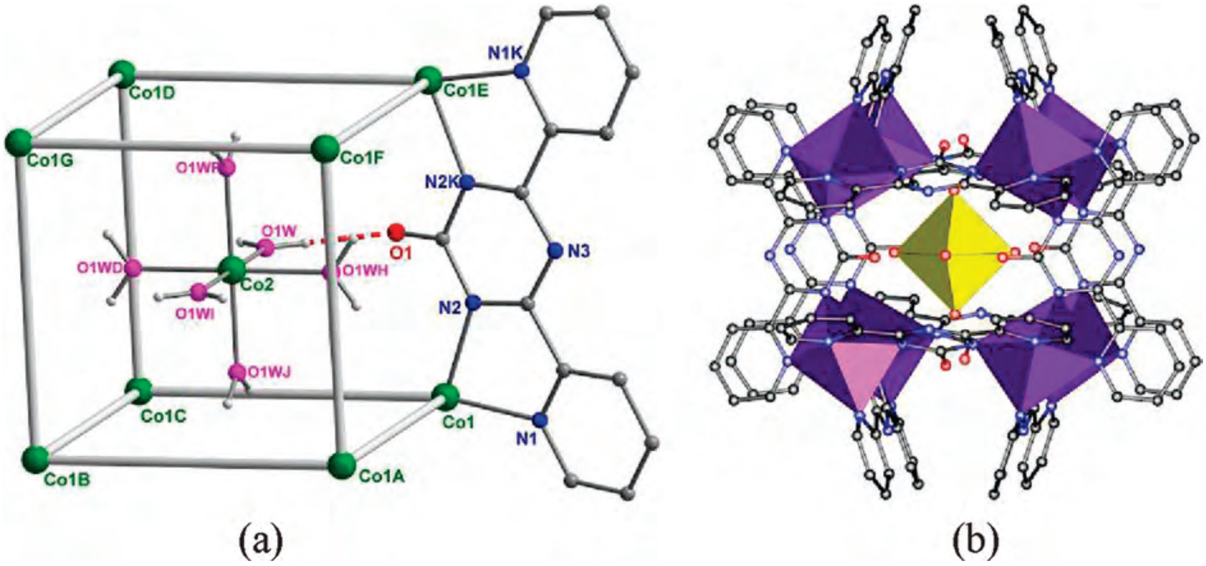

Figure 3. Views of the cationic structure of **2** with only one bridging ligand shown for clarity (a) and with polyhedrons for Co(II) ions (b). Symmetry code: A −*z*, *x*, *y*; B −*y*, −*z*, *x*; C *y*, −*z*, *x*; D *z*, −*x*, −*y*; E *y*, *z*, −*x*; F −*y*, *z*, −*x*; G −*x*, −*y*, −*z*; H *z*, *x*, *y*; I −*x*, −*y*, *z*; J *y*, *z*, *x*; K *x*, *y*, −*z*.

ligands, which arrange the ligands at the appropriate positions and further coordinate to metal ions to form the cubic structure (Scheme 3.)

To further detail the reaction conditions, five factors, such as the ratio of metal ion toward ligand, reaction temperature, different metal salts as the starting material, solvent, and pH value, were examined. First, when the ratio was fixed at 1:1, complex **1** was obtained in a good yield. However, the exact ratio of metal ion toward ligand in **1** is 3:4; therefore, various ratios from 3:1 to 1:2 were adopted. We found that the main

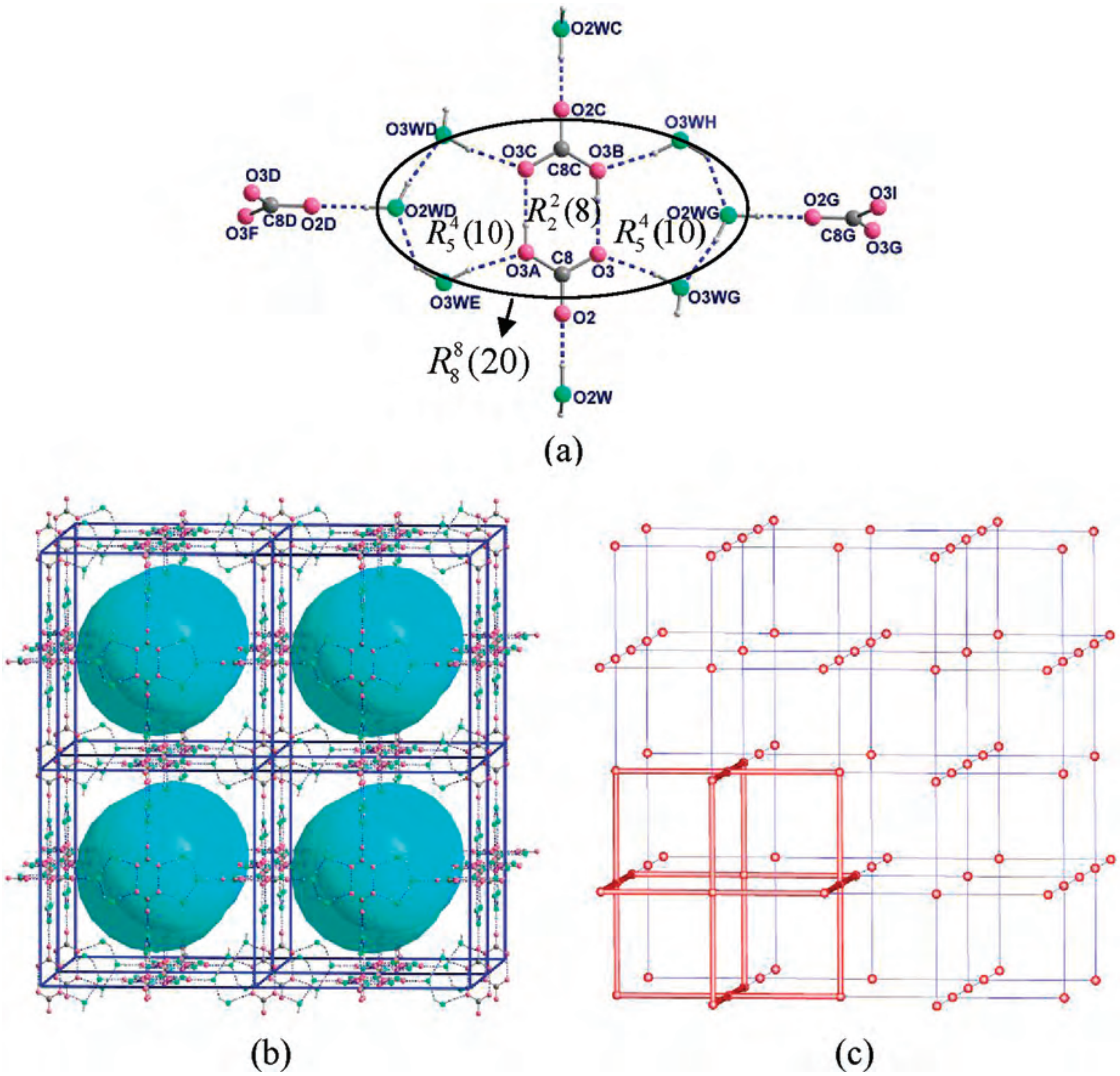

Figure 4. Views of the $R_8^8(20)$synthon (a), the 3D hydrogen-bonded host framework with the $[Co(H_2O)_6\subset Co_8(L1)_{12}]^{6+}$ cations (the cyan balls) as guests (b), and the NbO net (c, the red ball is the $R_8^8(20)$synthon and the $[Co(H_2O)_6\subset Co_8(L1)_{12}]^{6+}$ cations are omitted) in **2**. Symmetry codes: A $x, -y, z$; B $-x, y, 1 - z$; C $-x, -y, 1 - z$; D $-0.5 + z, -0.5 + x, 0.5 + y$; E $0.5 - z, -0.5 + x, 0.5 + y$; F $-0.5 + z, -0.5 + x, 0.5 - y$; G $0.5 - z, 0.5 - x, 0.5 - y$; H $-0.5 + z, 0.5 - x, 0.5 - y$; I $0.5 - z, 0.5 - x, 0.5 + y$.

product was **1** when the ratio varied from 3:1 to 3:4. In these cases, the excess of metal ion did not make notable influence on the yields of **1**, which were calculated on the basid of the amount of HL1. On the other hand, when the metal ion was in deficiency (from the ratios of 3:4 to 1:2), the ligand L1 prefered to coordinate in tridentate terpyridine-like mode and finally form the $Co(L1)_2$ species. Second, the optimal reaction temperature ranged from 110 to 120 °C, the high temperature (130 and 150 °C) induced low yield, concomitant with the appearance of many byproducts. Although **1** crystallized from the filtrate after about one week, the normal reflux approach with the same reaction materials and solvent did not afford the cubelike product, indicating that the solvothermal reaction was required in the present case. Third, other cobalt(II) salts were employed as the starting material. When $CoCl_2 \cdot 6H_2O$ was used as the source of metal salt, the same cubelike cation offered.[27] However, when $Co(CH_3CO_2)_2 \cdot 4H_2O$ or $CoSO_4 \cdot xH_2O$ was used, no cubic product was obtained in the present conditions. The observations seem to suggest that the source of the cobalt(II) salt may also affect on the formation of the cubelike structure. In addition, the mixture solvent is also necessary. No cubic product was obtained in the presence of the unique solvent such as water, methanol, and ethanol. Finally, the pH value effect on the reaction was also examined. We found that **1** was the main product in the pH 6−9 range. When the pH value was lower than 6, no product **1** was obtained; this may be attributed to the protonation of the phenol group and pyridyl group. At higher pH value, the ligand is unstable in the hydrothermal conditions.

The powder X-ray diffraction of the as-synthesized products of **1** and **2** give satisfactory XRD patterns (see

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(27) The unit cell was measured: crystal system, triclinic; space group, $P\bar{1}$; a = 18.086(5) Å, b = 18.178(8) Å, c = 18.543(5) Å, α = 67.87(3)°, β = 73.94(4)°, γ = 60.66(3)°, V = 4891(2) Å^3.

Figures S1 and S2 in the Supporting Information), which closely match with the simulated ones from the single-crystal data, respectively, indicating that the samples are in pure phase. Furthermore, thermal gravimetric analyses (TGA) were performed from 25 to 600 °C to examine the lattice water molecules and stability. For **1**, the weight loss of 5.4% in the range of 25−102 °C (see Figure S3 in the Supporting Information) corresponds to the loss of twelve lattice water molecules (calculated 5.1%), indicating that the guest water molecules were completely removed at 102 °C. When the temperature is increased to 300 °C, the weight loss of 7.1% corresponds to the loss of eighteen water molecules (calculated 7.6%, twelve lattice and six coordinated water molecules). For **2**, three steps were observed (see Figure S4 in the Supporting Information). First, from 25 to 96 °C, the weight loss of 9.5% corresponds to the loss of 24 lattice water molecules (calculated 9.7%). Second, the weight loss of 17.6% up to 200 °C corresponds to the loss of 24 lattice water molecules and six hydrogen carbonate anions (calculated 17.9%). Finally, when the temperature is increased to 340 °C, the six coordinated water were also lost with a weight loss of 20.7% (calculated 20.4%, 24 water, 6 HCO_3^-, and 6 coordinated water).

Crystal Structure and Magnetic Properties of 1. Complex **1** crystallizes in a centrosymmetric space group $P\bar{1}$ and consists of a cubic cluster $[Co(H_2O)_6 \subset Co_8(L1)_{12}]$, six nitrate anions, and twelve lattice water molecules that have been confirmed by elemental and TG analyses (see Figure S3 in the Supporting Information). X-ray diffraction reveals the cluster with an approximately cubic array of Co(II) ions at the corners and a bridging ligand L1 along each edge (see Figure 1a.) The Co•••Co distances along the edges are in a narrow range 6.297(2)−6.363(2) Å with angles at the corners varying between 89.5 and 90.9°. These are comparable to the Ni(II) cube reported by Eddaoudi and his co-workers.[10i] The cubic ion lies on an inversion center; therefore, only four Co(II) ions are crystallographically unique (see Figure 1b). Each vertical Co(II) ion is coordinated to six nitrogen atoms from three separate ligands, producing the *facial* octahedral coordination geometry. The bond length of Co−N all lie in the range of 2.119(6)−2.165(6) Å, and the bite angles are in a narrow range of 76.0(2)−77.4(2)°. The distance from the cube center to the closet atom of L1 O1 is 4.20 Å; thus the inner cavity has an estimated volume of ~180 $Å^3$, obtained by subtraction of the van der Waals radius of the oxygen atoms. A $[Co(H_2O)_6]^{2+}$ cation with an ideal octahedralgeometry(Co−O=2.058(5)−2.067(5)Åand∠O1W−Co−O2W = 90°) locates in the center of the cubic cluster as a guest to assemble into the cubic structure. Furthermore, the hydrate ion forms 12-fold strong hydrogen bonds (Ow•••O = 2.659(1)−2.692(1) Å, ∠Ow−H•••O = 156.3(4)−174.2(4)°) with the twelve oxygen atoms from twelve L1 ligands.

The magnetic susceptibility of **1** has been investigated in the temperature range of 2−320 K, and the plots of $\chi_M T$ and χ_M^{-1} versus T are shown in Figure 2. The $\chi_M T$ exhibits a continuous decrease upon cooling from ca. 22.10 $cm^3\ mol^{-1}$ K (13.30 μ_B) at 300 K to ca. 2.87 $cm^3\ mol^{-1}$ K (4.79 μ_B) at 2 K because of antiferromagnetic coupling. The temperature dependence of magnetic susceptibilities on the range of 7−300 K obeys the Curie−Weiss law $\chi_M = C/(T - \theta)$. The $1/\chi_M$ versus T plot gives a Weiss constant $\theta = -19.83$ K and a Curie constant $C = 23.67\ cm^3\ mol^{-1}$ K, indicating a moderate antiferromagnetic coupling between the metallic centers along the bridged ligand. At room temperature, the $\chi_M T$ value is 22.10 $cm^3\ mol^{-1}$ K (13.30 μ_B), which is much higher than the calculated value [16.87 $cm^3\ mol^{-1}$ K (11.62 μ_B)] for the nine isolated Co(II) ions ($S = 3/2$, $g = 2.0$), indicating that a significant orbital contribution is occurred. The magnetism of high-spin Co(II) centers ($S_i = 3/2$), as in the cube complex **1**, is notoriously difficult to describe because of spin−orbital coupling.[28]

Crystal Structure of 2. When complex **1** was added to an aqueous solution of potassium carbonate or potassium hydrogen carbonate, complex **2** was obtained. It crystallizes in a high symmetric space group $Im\bar{3}$, much different from that of **1**. It consists of a cubic cluster $[Co(H_2O)_6 \subset Co_8(L1)_{12}]^{6+}$, six hydrogen carbonate anions, and 24 lattice water molecules. The X-ray single-crystal structural analysis shows the cluster with an ideally cubic array of Co(II) ions at the corners and a bridging ligand L1 along each edge with a Co•••Co distance 6.329(2) Å along the edge (see Figure 3.) The other structural properties are very similar to those of **1** and are given in Tables 2 and 3.

The most interesting observation is each hydrogen carbonate anion provides one donor and one acceptor site to form a planar dimer motif $R_2^2(8)$ synthon[29] via two robust hydrogen bonds (O3•••O3B = 2.61(1) Å, ∠O3−H3B•••O3B = 180°) (see Figure 4.) The four acceptor sites of each dimer are hydrogen-bonded acceptors from four water molecules (O3•••O3W = 2.66(1) Å), which further connected by two water molecules (O2W•••O3W = 2.71(1) Å) into a pair of $R_5^4(10)$ synthons. Thus, each $[(HCO_3)_2]^{2-}$ dimer and six water molecules constitute a planar supramolecular synthon $R_8^8(20)$. Moreover, these $R_8^8(20)$ synthons connect each other in vertical fashion via the formation of four strong hydrogen bonds between the two terminal oxygen of hydrogen carbonate anion and the two oxygens from water (O2W•••O2 = 2.52(2) Å, ∠O2W−H2wA•••O2 = 180°) generating a 3D hydrogen-bonded host framework. Here the $R_8^8(20)$ synthon can be regarded as a four connector leading to a classical NbO net with cubelike host cavities of ~20 Å diameter that are filled by the cubelike $[Co(H_2O)_6 \subset Co_8(L1)_{12}]^{6+}$ cations as guests. Therefore the cubelike, nanocage $[Co(H_2O)_6 \subset Co_8(L1)_{12}]^{6+}$ cations can be considered as templates in the formation of the 3D NbO net. Although the $[(HCO_3)_2]^{2-}$ synthon has been widely found and used in hydrogen-bonded architecture in crystal engineering,[30] the assembly into 3D hydrogen-bonded host framework is very rare.[31]

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Conclusion

Two new complexes with a cubelike motif, assembled by eight cobalt ions at the corners and twelve bis-bidentate ligands L1 as the edges, have been synthesized. The $[Co(H_2O)_6]^{2+}$ ion is encapsuled in the central cavity of the cubelike nanocage $[Co(H_2O)_6 \subset Co_8(L1)_{12}]^{6+}$ cation via the formation of strong hydrogen bonding between the coordinated water molecules and the oxygen atoms of L1 as a guest. A new, planar supramolecular synthon $R_8^8(20)$, based on a $[(HCO_3)_2]^{2-}$ dimer and six lattice water molecules, is constructed and assembled into a 3D hydrogen-bonded NbO net in the presence of the cubelike nanocage with $[Co(H_2O)_6 \subset Co_8(L1)_{12}]^{6+}$ cations as templates.

Acknowledgment. This work was supported by the NSF of China (No. 20771104) and Guangdong Province (No. 20623086), the Doctoral Programs Foundation of Ministry of Education of China (No. 20070558009), and the National Foundation for Fostering Talents of Basic Science (No. J0730420).

Supporting Information Available: XRD, TGA, and X-ray crystallographic file in CIF format for the structure determination of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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