Inorg. Chem. **2006**, *45*, 8098–8107

Inorganic Chemistry
Article

Cadmium(II) and Copper(II) Complexes with Imidazole-Containing Tripodal Polyamine Ligands: pH and Anion Effects on Carbon Dioxide Fixation and Assembling

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Received April 3, 2006

A new Cd(II) complex $[Cd_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4\cdot 2CH_3CN$ (**1**) with two-dimensional (2D) network structure was obtained by reaction of an imidazole-containing tripodal polyamine ligand *N*^{1}-(2-aminoethyl)-*N*^{1}-(2-imidazolethyl)-ethane-1,2-diamine (L) with $Cd(ClO_4)_2\cdot 6H_2O$ at pH 9.0 in air. The carbonate anions (CO_3^{2-}) are from the hydration of the atmospheric carbon dioxide, which is the same as in the previously reported Cu(II) complex $[Cu_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4\cdot 3CH_3CN$ (**2**). However, the coordination mode of CO_3^{2-} in **1** is $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ while the one in **2** is $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$. One-dimensional (1D) chain Cd(II) and Cu(II) complexes $[Cd(L)Cl]ClO_4\cdot H_2O$ (**3**) and $[Cu(L)(H_2O)](ClO_4)_2$ (**4**) without CO_3^{2-} were prepared by a similar method as that for **1** and **2** except for the different reaction pH, namely, **3** and **4** were obtained at pH 7 while **1** and **2** were obtained at pH 9. In addition, when $Cu(NO_3)_2$ was used to react with L at pH 9, a unique 1D double-stranded helical chain complex $[Cu(L)Cl]NO_3\cdot 1.25H_2O$ (**5**) was obtained. The results revealed that the reaction pH and the counteranion have great impact on the carbon dioxide absorption and hydration as well as on the assembling and structure of the complexes. The magnetic property of complex **2** was investigated in the temperature range of 1.8–300 K, and weak ferromagnetic coupling among the $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{–}CO_3^{2-}$ bridged Cu(II) atoms was observed.

Introduction

Over the past years, the capture, activation, and conversion of small molecules such as carbon dioxide (CO_2), methane, dioxygen, and so forth has drawn much attention.[1] Part of such a kind of research work has dealt with the insertion CO_2 from the atmosphere, particularly as carbonate anion (CO_3^{2-}), into coordination complexes.[2] As a result of the variety of the coordination mode of the carbonate anion, extended metal−carbonato complexes, such as dimers, trimers, even tetramers, and one- (1D) and two-dimensional (2D) systems have been reported.[3] Such kind of metal−carbonato complexes are important in bioinorganic fields with relation to Zn(II) complexes as a model of carbonic anhydrases.[4] In addition, Cu(II)− and Ni(II)−carbonato complexes have been prepared as analogues of Zn(II), and

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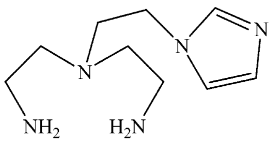
10.1021/ic0605524 CCC: $33.50

Scheme 1



L

their magnetic properties have been studied.[5] However, Cd(II)−carbonato coordination chemistry has received less attention up to now although the Cd(II) ion is also important in bioinorganic research, for example, Cd(II) substituted binuclear zinc(II) hydrolytic enzymes for the favorableness of NMR studies.[6]

In our previous studies, we found that the imidazole-containing ligands are versatile and can offer a variety of metal complexes with interesting structures and properties when they react with metal salts.[7] Recently, we prepared a new imidazole-containing tripodal polyamine ligand N^1-(2-aminoethyl)-N^1-(2-imidazolethyl)-ethane-1,2-diamine (L; Scheme 1), and its reactions with $M(ClO_4)_2 \cdot 6H_2O$ [M = Cu(II), Zn(II)] were carried out. It is interesting to find that 2D networks were formed with the aid of CO_3^{2-} anions which come from the absorption and hydration of the atmospheric carbon dioxide.[3e] As an extension of such research work, ligand L was used to react with $Cd(ClO_4)_2 \cdot 6H_2O$ to give complex $[Cd_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4 \cdot 2CH_3CN$ (**1**) with 2D network structure, which was compared with the previously reported Cu(II) complex $[Cu_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4 \cdot 3CH_3CN$ (**2**).[3e] In addition, to further investigate the influence of reaction pH and the counteranion on the structure of complexes as well as on the absorption of carbon dioxide from air, reactions of L were carried out with $Cd(ClO_4)_2 \cdot 6H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$ at pH 7 and $Cu(NO_3)_2 \cdot 3H_2O$ at pH 9, respectively, and complexes $[Cd(L)Cl]ClO_4 \cdot H_2O$ (**3**), $[Cu(L)(H_2O)](ClO_4)_2$ (**4**), and $[Cu(L)Cl]NO_3 \cdot 1.25H_2O$ (**5**) were obtained. Herein we report the crystal structure of complexes **1**, **3**, **4**, and **5** and a discussion of the effect of metal ions, reaction pH, and counteranion on the structure of the complexes as well as the magnetic property of **2**.

Experimental Section

General Materials and Instruments. All the reagents are of analytical grade from commercial sources and all solvents were distilled or dried when necessary by general procedures. The ligand N^1-(2-aminoethyl)-N^1-(2-imidazolethyl)-ethane-1,2-diamine (L) was prepared as previously reported.[3e] Elemental analyses for C, H, and N were made on a Perkin-Elmer 240C elemental analyzer at the Analysis Center of Nanjing University. Magnetic measurements for complex **2** in the range of 1.8−300 K were performed in an MPMS−SQUID magnetometer at a field of 2000 G on powder samples in a Teflon capsule. The diamagnetic contributions of the samples were corrected by using Pascal's constants. Thermogravimetric analysis (TGA) was conducted on a Pyris 1 TGA analyzer in a nitrogen atmosphere in the range of 25 to 700 °C with a heating rate of 20 °C/min at the Analysis Center of Nanjing University. X-ray powder diffraction (XRPD) patterns were recorded on a Lab X-ray 6000 diffractometer with graphite-monochromatic Cu Kα ($\lambda = 1.54$ Å) radiation at room temperature.

Preparation of the Complexes. $[Cd_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4 \cdot 2CH_3CN$ (1). The title complex was prepared in 70% yield by the same method as reported for complex **2** in the literature[3e] using $Cd(ClO_4)_2 \cdot 6H_2O$. Anal. Calcd for $C_{30}H_{57}Cd_3Cl_4N_{15}O_{19}$ (noncoordinated CH_3CN molecules were lost upon drying): C, 24.25; H, 4.14; N, 15.15. Found: C, 24.28; H, 4.28; N, 14.95.

$[Cd(L)Cl]ClO_4 \cdot H_2O$ (3). $L \cdot 4HCl$ (0.0343 g, 0.1 mmol) and $Cd(ClO_4)_2 \cdot 6H_2O$ (0.0419 g, 0.1 mmol) were mixed in 5 mL of water. Then the pH of the solution was adjusted to 7 by addition of 0.5 M NaOH. After stirring for 2 h, the solution was filtrated. Colorless platelet single crystals were obtained in 3 days by slow evaporation of the solvent in 50% yield. Anal. Calcd for $C_9H_{21}Cl_2CdN_5O_5$: C, 23.37; H, 4.57; N, 15.14. Found: C, 23.32; H, 4.48; N, 15.17.

$[Cu(L)(H_2O)](ClO_4)_2$ (4). To an aqueous solution (5 mL) of $L \cdot 4HCl$ (0.0343 g, 0.1 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0371 g, 0.1 mmol) in water (5 mL) was added dropwise with stirring. The pH of the solution was adjusted to 7 by addition of 0.5 M NaOH. After the addition of 2 mL of saturated $NaClO_4$, the blue precipitate appeared. Then 5 mL of CH_3CN was added to give a clear solution. Blue platelet single crystals were obtained in 1 week by slow evaporation of the solvent in 65% yield. Anal. Calcd for $C_9H_{21}Cl_2CuN_5O_9$: C, 22.63; H, 4.43; N, 14.66. Found: C, 22.64; H, 4.38; N, 14.51.

$[Cu(L)Cl]NO_3 \cdot 1.25H_2O$ (5). $L \cdot 4HCl$ (0.0343 g, 0.1 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (0.0242 g, 0.1 mmol) were mixed in 5 mL of water. In addition, 0.5 M NaOH solution was added dropwise to adjust the solution pH value to 9. After the mixture was stirred for 2 h at room temperature, it was filtered. Blue block crystals were obtained in 50% yield by slow diffusion of ethanol into the filtrate after 7 days. Anal. Calcd for $C_9H_{21.5}CuClN_6O_{4.25}$: C, 28.39; H, 5.69; N, 22.07. Found: C, 28.74; H, 5.68; N, 22.27.

Caution: *Perchlorate salts of compounds containing organic ligands are potentially explosive and should be handled with care.*

Crystallography. The data collection for complexes **1** and **4** was carried out on a Rigaku RAXIS−RAPID Imaging Plate diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) at 200 K. The structures were solved by direct method with SIR92[8] and expanded using Fourier techniques.[9] The absorption correction for the complexes was carried out by the multiscan method. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2. The hydrogen

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Table 1. Crystallographic Data for Complexes **1**, **3**, **4**, and **5**

complex	**1**	**3**
empirical formula	$C_{32}H_{63}Cd_3Cl_4N_{17}O_{19}$	$C_9H_{21}Cl_2CdN_5O_5$
formula weight	1468.99	462.21
crystal system	trigonal	monoclinic
space group	$P3c1$	$P2_1$
a (Å)	13.749(2)	9.2743(14)
b (Å)	13.749(2)	7.6104(11)
c (Å)	16.889(3)	11.8112(18)
α (deg)	90	90.00
β (deg)	90	104.755(3)
γ (deg)	120	90.00
V (Å^3)	2764.8(8)	806.2(2)
Z	2	2
T (K)	200	293
D_{calcd} (g cm^{-3})	1.765	1.906
μ (mm^{-1})	1.419	1.715
2θ max (deg)	55.0	56.0
R_{int}	0.0822	0.0292
R [$I > 2\sigma(I)$]^a	0.0430	0.0682
wR [$I > 2\sigma(I)$]^b	0.1006	0.1646

complex	**4**	**5**
empirical formula	$C_9H_{21}Cl_2CuN_5O_9$	$C_9H_{21.5}ClCuN_6O_{4.25}$
formula weight	477.75	380.806
crystal system	monoclinic	tetragonal
space group	$P2_1/c$	$P4_2/n$
a (Å)	10.607(6)	22.477(3)
b (Å)	9.852(6)	22.477(3)
c (Å)	16.643(10)	6.4602(11)
α (deg)	90.00	90.00
β (deg)	90.37(5)	90.00
γ (deg)	90.00	90.00
V (Å^3)	1739.2(18)	3263.8(8)
Z	4	2
T (K)	200	293
D_{calcd} (g cm^{-3})	1.825	1.556
μ (mm^{-1})	1.620	1.529
2θ max (deg)	55.0	56.0
R_{int}	0.0561	0.0630
R [$I > 2\sigma(I)$]^a	0.0295	0.0603
wR [$I > 2\sigma(I)$]^b	0.0667	0.1370

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR $= |\sum w(|F_o|^2 - |F_c|^2)|/\sum|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

atoms except for those of water molecules were generated geometrically. All calculations were carried out on a SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation.[10] Diffraction data of complexes **3** and **5** were collected on a Bruker SMART CCD system equipped with monochromated Mo Kα radiation (λ = 0.710 73 Å) at 293 K. The data integration and empirical absorption corrections were carried out by SAINT programs.[11] The structures were solved by direct method (SHELXS 97).[12] All non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares techniques (SHELXS 97).[12] Atom O1W in **5** has two positions with the site occupancy factors of 0.63(2) and 0.37(2), respectively. The hydrogen atoms except for those of water molecules were generated geometrically. Details of the crystal parameters, data collection, and refinements for the complex are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are given in Table 2.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**, **3**, **4**, and **5**^{a}

	1		
Cd1−N3	2.273(6)	Cd1−O1$^{\#2}$	2.546(4)
Cd1−N2	2.274(5)	Cd1−O1	2.329(4)
Cd1−N12$^{\#1}$	2.257(4)	Cd1−N1	2.553(5)
N12$^{\#1}$−Cd1−N3	108.1(2)	N3−Cd1−O1$^{\#1}$	86.54(17)
N12$^{\#1}$−Cd1−N2	110.70(18)	N2−Cd1−O1$^{\#1}$	74.77(15)
N3−Cd1−N2	136.0(2)	O1−Cd1−O1$^{\#1}$	54.31(17)
N12$^{\#1}$−Cd1−O1	92.02(15)	N12$^{\#1}$−Cd1−N1	108.29(18)
N3−Cd1−O1	85.87(16)	N3−Cd1−N1	74.45(18)
N2−Cd1−O1	112.33(15)	N2−Cd1−N1	74.39(17)
N12$^{\#1}$−Cd1−O1$^{\#2}$	142.92(16)	O1−Cd1−N1	155.14(14)
O1$^{\#2}$−Cd1−N1	108.43(15)		
	3		
Cd1−N1	2.502(9)	Cd1−N3	2.377(13)
Cd1−N2	2.254(11)	Cd1−N5	2.248(9)
Cd1−Cl1	2.527(9)		
N5$^{\#3}$−Cd1−N2	100.6(4)	N5$^{\#3}$−Cd1−N3	87.4(5)
N2−Cd1−N3	99.0(5)	N5$^{\#3}$−Cd1−N1	159.6(4)
N5$^{\#3}$−Cd1−Cl1	98.3(4)	N2−Cd1−Cl1	155.2(3)
N3−Cd1−Cl1	97.8(4)	N1−Cd1−Cl1	92.6(3)
N2−Cd1−N1	74.7(3)		
	4		
Cu1−N1	2.0156(2)	Cu1−N3	2.0293(2)
Cu1−N2	2.0305(2)	Cu1−N12	1.9677(2)
Cu1−O1	2.353(2)		
N12−Cu1−N1	180.0	N12−Cu1−N3	95.91(8)
N1−Cu1−N3	84.54(8)	N12−Cu1−N2	95.72(9)
N1−Cu1−N2	84.58(8)	N3−Cu1−N2	168.18(7)
N12−Cu1−O1	94.98(8)	N1−Cu1−O1	97.89(8)
N3−Cu1−O1	87.60(8)	N2−Cu1−O1	89.35(8)
	5		
Cu1−N2	1.998(4)	Cu1−N11$^{\#4}$	2.001(3)
Cu1−N3	2.016(4)	Cu1−N1	2.076(3)
Cu1−Cl1	2.5485(13)		
N2−Cu1−N11$^{\#4}$	93.91(14)	N2−Cu1−N3	162.53(17)
N11$^{\#4}$−Cu1−N3	94.09(15)	N2−Cu1−N1	84.79(14)
N11$^{\#4}$−Cu1−N1	163.71(14)	N3−Cu1−N1	83.18(14)
N2−Cu1−Cl1	97.89(12)	N11$^{\#4}$−Cu1−Cl1	91.48(10)
N3−Cu1−Cl1	97.40(13)	N1−Cu1−Cl1	104.79(10)

^{a} Symmetry transformations used to generate equivalent atoms: #1, $-x + y$, $-x + 1$, z; #2, $-x + y + 1$, $-x + 1$, z; #3, $1 - x$, y, z; and #4, $1 - y$, $x - 1/2$, $z - 1/2$.

Results and Discussion

Description of Crystal Structures. $[Cd_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4 \cdot 2CH_3CN$ (1). Crystallographic analysis revealed that complex **1** crystallizes in the trigonal space group $P3c1$ with the compositions of a $[Cd_3(L)_3(\mu_3\text{-}CO_3)]^{4+}$ cation, four perchlorate anions, and two acetonitrile molecules. As shown in Figure 1a, each Cd(II) atom is six-coordinated by four N atoms from two different L ligands and two O atoms from the coordinated CO_3^{2-}. The bond lengths of Cd−N are in the range from 2.257(4) to 2.553(5) Å, and the ones of Cd−O are 2.329(4) and 2.546(4) Å; the coordination angles around the Cd(II) atom are from 54.31(17) to 155.14(14)° (Table 2). Therefore, the coordination geometry of the Cd(II) atom can be regarded as a strongly distorted octahedron due to the chelating coordination of two O atoms of the carbonato ligand. On the other hand, each ligand L in turn bridges two Cd(II) centers, and three Cd(II) atoms connect three L ligands to generate a M_3L_3 21-membered trigonal ring (Figure 1a) which is the same as that observed in complex **2**.[3e] The trigonal rings are further linked together by CO_3^{2-} to generate a 2D network (Figure 1b). The CO_3^{2-} anions in **1** are from the absorption and hydration of atmospheric carbon dioxide

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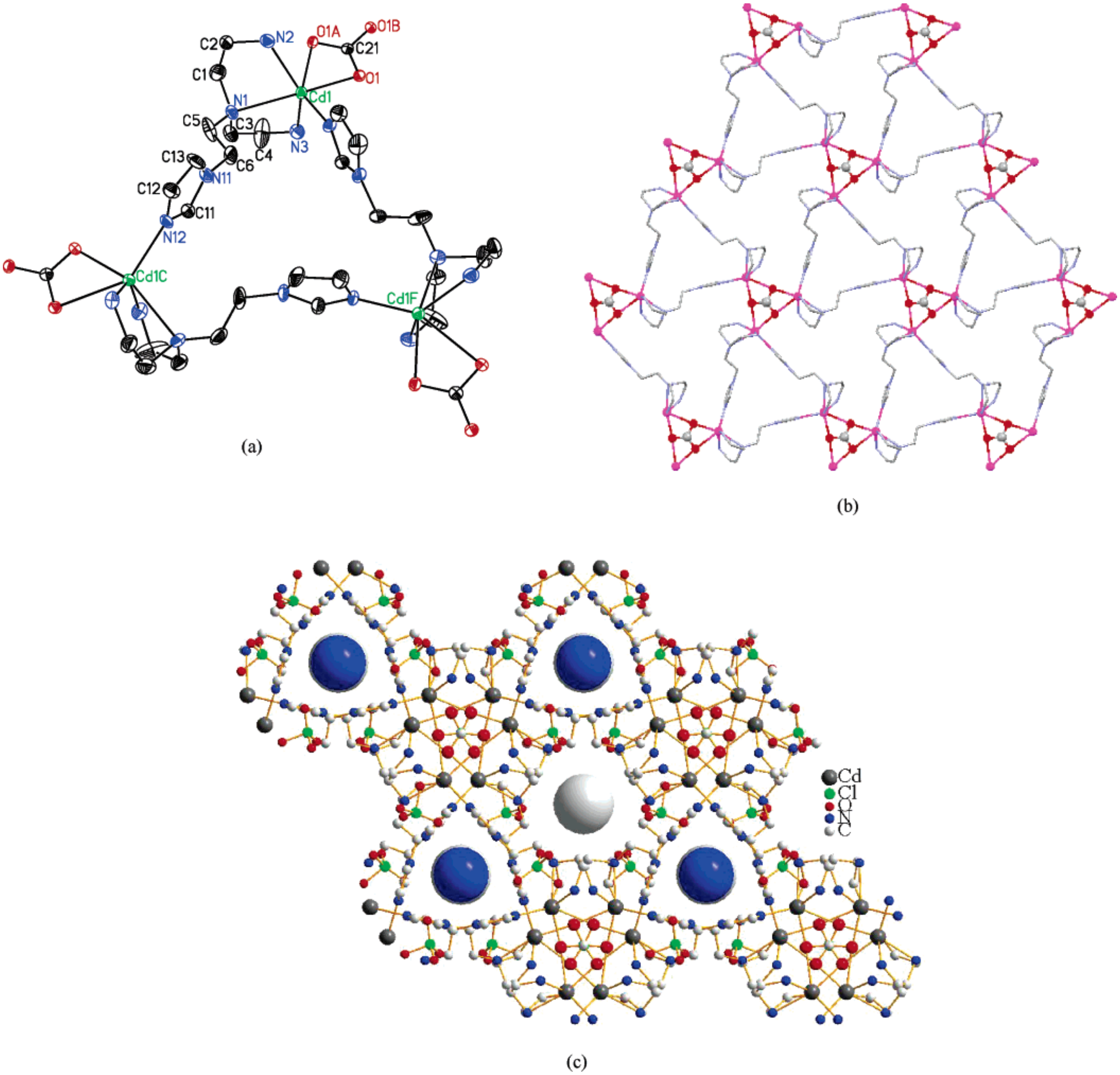

Figure 1. (a) ORTEP plot of coordination environment of Cd(II) centers in **1**, with thermal ellipsoids at 30% probability; hydrogen atoms were omitted for clarity. (b) The 2D network structure formed by bridging carbonate anions in **1**; water molecules are omitted for clarity. (c) The packing structure of complex **1** along the *c* axis with CH_3CN molecules (in space-filling mode, blue and gray refer to the N and C atoms of CH_3CN, respectively) in the trigonal channels and perchlorate anions lying between layers.

as demonstrated for Cu(II) complex **2**.[3e] However, it is worth noting that the carbonate anions here adopt a μ_3-η^2:η^2:η^2-tridentate bridging mode, rather than a μ_3-η^1:η^1:η^1-tridentate one as observed in complex **2** because the coordinated Cu−O bond distance is 1.974(2) Å while the separation between the Cu(II) and the adjacent uncoordinated O atom is 2.916 Å as schematically shown in Scheme 2.[3e] The μ_3-η^2:η^2:η^2-coordination mode of CO_3^{2-} is rare in the literature. Another example with such coordination mode of CO_3^{2-} was found in complex $[Cd_3(cyclam)_3(CO_3)](ClO_4)_4 \cdot 3H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).[6b] The Cd−O bond lengths of 2.329(4) and 2.546(4) Å and the O1−Cd1−O1A bond angle of 54.31(17)° in complex **1** (Table 2) are similar to those observed in $[Cd_3(cyclam)_3(CO_3)](ClO_4)_4 \cdot 3H_2O$.[6b] Although di- and tri-nuclear Cd(II)−carbonato complexes have been reported in the literature,[6] to the best of our knowledge,

Scheme 2. Modes of Carbonato Coordination in Complex **1** (a) and Complex **2** (b)

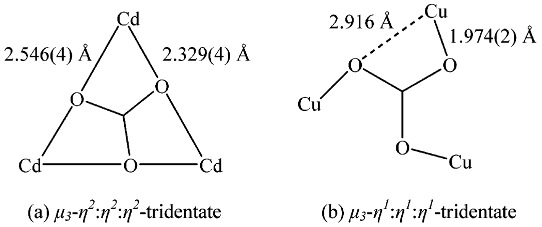

Table 3. Hydrogen Bonds Data for Complexes **1**, **3**, **4** and **5**[a]

D−H···A[b]	distance of D···A[b] (Å)	angle of D−H−A[b] (deg)
	1	
N2−H1···O24$^{\#1}$	3.190(3)	157
N2−H2···O11$^{\#1}$	3.093(7)	145
N3−H3···O12	3.170(7)	172
N3−H4···O23	3.360(3)	166
C2−H7···O22$^{\#1}$	3.340(2)	139
C4−H12···O24$^{\#2}$	2.990(6)	155
C5−H14···O21$^{\#3}$	3.402(3)	156
C11−H17···O23$^{\#3}$	3.210(2)	175
C13−H19···O22$^{\#1}$	3.360(3)	141
	3	
N2−H2A···O1′	3.074(19)	168
N3−H3D···O3′$^{\#4}$	2.54(3)	135
C1−H1B···O1W$^{\#5}$	3.48(6)	157
C3−H3B···Cl1′$^{\#6}$	3.051(18)	123
C3−H3C···O2′$^{\#7}$	3.08(3)	130
C6−H6B···Cl1′	3.53(2)	155
C7−H7A···O4′$^{\#8}$	3.06(3)	142
C9−H9A···O3′$^{\#9}$	3.20(2)	133
	4	
O1−H1···O13	2.896(3)	161
O1−H2···O12$^{\#10}$	2.895(3)	174
N2−H3···O11$^{\#11}$	3.146(3)	122
N2−H3···O23$^{\#11}$	3.061(3)	144
N2−H4···O14$^{\#10}$	3.116(3)	166
N3−H5···O13	3.127(3)	137
N3−H6···O22$^{\#12}$	3.109(3)	152
C1−H8···O24$^{\#10}$	3.123(3)	127
C5−H16···O21$^{\#12}$	3.492(3)	162
C6−H18···O14$^{\#11}$	3.377(3)	154
C11−H19···O12$^{\#10}$	3.407(3)	149
C12−H20···O21$^{\#12}$	3.321(3)	137
	5	
N2−H1A···O4$^{\#13}$	3.101(5)	165
N2−H1B···O2	3.101(5)	159
N2−H1B···O3	3.269(6)	137
N3−H3A···O1W$^{\#13}$	3.210(16)	138
N3−H3B···Cl1$^{\#13}$	3.225(4)	153
C11−H15A···Cl1$^{\#14}$	3.656(5)	170
C13−H16A···O2$^{\#15}$	3.377(5)	171

[a] Symmetry transformations used to generate equivalent atoms: #1, $1 - y$, $1 - x$, $1/2 + z$; #2, $1 - x + y$, $1 - x$, z; #3, $1 - y$, $1 + x - y$, z; #4, $-x$, $-1/2 + y$, $1 - z$; #5, $1 + x$, y, z; #6,$1 - x$, $-1/2 + y$, $2 - z$; #7, $1 - x$, $-1/2 + y$, $1 - z$; #8, $1 - x$, $1/2 + y$, $1 - z$; #9, $1 + x$, y, $1 + z$; #10, $1 - x$, $1 - y$, $1 - z$; #11, x, $-1 + y$, z; #12, $-x$, $-1/2 + y$, $3/2 - z$; #13, x, y, $-1 + z$; #14, $1/2 + y$, $1 - x$, $-1/2 + z$; and #15, $3/2 - y$, x, $3/2 - z$. [b] D = donor and A = acceptor.

complex **1** is the first example of a 2D network formed by the coordination of Cd(II) with carbonate until now.

The cationic layers of **1** are packed together in an ABAB fashion along the *c* axis to form trigonal channels filled with acetonitrile molecules (Figure 1c) as that in complex **2**. However, the acetonitrile molecules are not stable enough and are easy to lose upon drying probably due to no interactions such as hydrogen bonding between the acetonitrile and 2D network. In addition, the perchlorate anions are located between the cationic layers through the N−H···O and C−H···O hydrogen bonds between the 2D layers and the perchlorate anions. The hydrogen bonding data are listed in Table 3.

It is noteworthy that though both complex **1** and complex **2** have 2D network structure, they are not isomorphous. In addition to the different space group and the different coordination mode of CO_3^{2-} as mentioned above, there are two acetonitrile molecules in **1**, while complex **2** has three. Such difference is attributable to the different packing of the acetonitrile molecules in the 1D channel of the complexes. The CH_3CN molecules in **2** packed much closer than those in **1**, because the distances between the C atom of one CH_3CN and the N atom of the adjacent one are 5.75 and 3.65 Å in **1** and **2**, respectively.

[Cd(L)Cl]ClO$_4$·H$_2$O (3). To probe the effect of reaction pH on the fixation of CO_2 and the structure of the complexes, the reaction of ligand L with $Cd(ClO_4)_2·6H_2O$ at pH 7 was performed to give complex **3**. The single-crystal structure analysis revealed that complex **3** features a 1D zigzag chain structure rather than a 2D network observed in **1**, and it is clear that no CO_3^{2-} was found in complex **3**. In other words, no absorption of carbon dioxide from air occurred at pH 7. The coordination environment around the Cd(II) atom is shown in Figure 2a. Each Cd(II) atom is five-coordinated by three amine N atoms from a ligand, one imidazole N atom from another ligand, and one terminal Cl^- anion. It has been reported that such pentacoordinated geometry is assigned based on the τ value defined by Addison et al. ($\tau = 0$, for an ideal square pyramid, and $\tau = 1$, for a perfect trigonal bipyramid),[13] and the τ value of 0.073 for complex **3** suggests that the geometry around the Cd(II) center is a slightly distorted square pyramid. The basal plane is defined by the N1, N2, N3, and N5A atoms, while the apical position is occupied by the Cl1 atom. The Cd(II) centers were extended to form an infinite 1D chain structure by the bridging connection of the ligands L (Figure 2a). The 1D chains of **3** are further connected by C−H···Cl hydrogen bonds among the chains, and N−H···O and C−H···O hydrogen bonds between the ligand and perchlorate O atoms and water molecule O atoms (Table 3) to generate three-dimensional (3D) framework structure as shown in Figure 2b.

[Cu(L)(H$_2$O)](ClO$_4$)$_2$ (4). Complex **4** was also obtained at pH 7 by reaction of ligand L with $Cu(ClO_4)_2·6H_2O$ and compared with complex **2**. The structure analysis showed that complex **4** has a 1D zigzag chain structure similar to that of complex **3**, which is different from the 2D network structure of complex **2**. The results further confirm that no absorption of carbon dioxide from air occurred at pH 7. As clearly shown in Figure 3a, each Cu(II) atom is five-coordinated by four N atoms from two ligands and one O atom of a water molecule. A τ value of 0.197 for complex **4** suggests that the Cu(II) center adopts a distorted square pyramid coordination geometry. The basal plane is defined by the N1, N2, N3, and N12 atoms, while the apical position is occupied by O1. On the other hand, the ligand L also bridges two Cu(II) centers by all of its N donor atoms to give an infinite 1D chain structure (Figure 3a). In addition, the 1D chains of **4** were further connected by O−H···O, N−H···O, and C−H···O hydrogen bonds between the coordinated water molecule and perchlorate O atoms and between the C−H or N−H of the ligand L and the perchlorate anions (Table 3) to generate 2D network structure as shown in Figure 3b.

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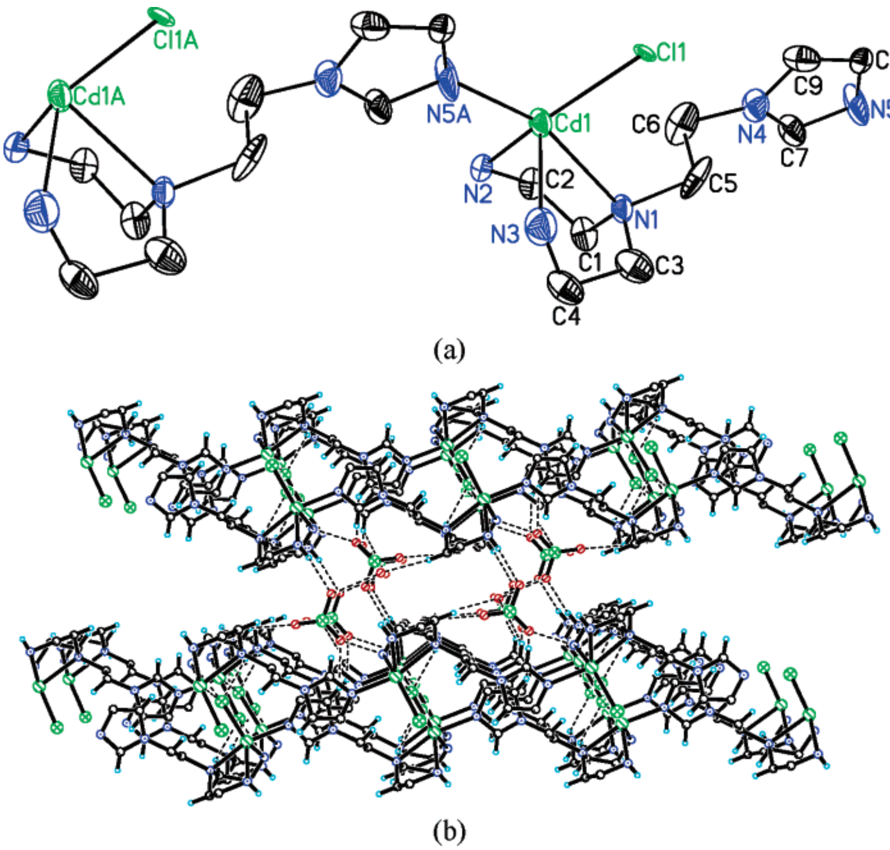

Figure 2. (a) Cationic 1D chain structure of **3** with atom numbering scheme (hydrogen atoms were omitted for clarity). (b) 3D network formed by hydrogen bonding indicated by the dashed line, packed along the *a* axis of **3**.

It is interesting that when ligand L reacted with $Cd(ClO_4)_2 \cdot 6H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$ at pH 9, simultaneous absorption and hydration of atmospheric carbon dioxide occurred and complexes **1** and **2** were isolated. The results imply that the reaction pH has great influence on the carbon dioxide absorption and hydration as well as on the structure of the complexes.

[Cu(L)Cl]$NO_3 \cdot 1.25H_2O$ (5). In addition to the reaction pH, the effect of the counteranion was also investigated by reaction of ligand L with $Cu(NO_3)_2 \cdot 3H_2O$ to give complex **5**, and the comparison of complex **2** with perchlorate anions and complex **5** with nitrate anions was carried out. Crystallographic analyses provide direct evidence that the structure of **5** is different from that of **2**. Complex **5** consists of cationic unit $[Cu(L)Cl]^+$, a nitrate anion, and lattice water molecules. As illustrated in Figure 4a, each Cu(II) atom is also five-coordinated by four N atoms from two different ligands L and one Cl^- anion (originated from L·4HCl) in a slightly distorted square pyramid indicated by a τ value of 0.021.[13] Namely, the coordination environments around the Cu(II) in **2** and **5** are different; the former one has a N_4O donor set in which the O atom comes from CO_3^{2-} while the latter one has a N_4Cl binding set. Linked by ligands L, the Cu(II) centers are expanded to right-handed and left-handed cationic helical chains which intertwined with each other to form unique double-stranded helical chain structure running along the crystallographic 4_2 axis in the *a* direction as shown in Figure 4b. The pitch of the helical chain is 12.92 Å (equal to 2*c* of the unit cell), containing four Cu(II) atoms per turn.

The results indicate that the counteranions have significant effect on the polymer assembling and thus on the structure of the complexes. L·4HCl was also used in the preparation of complex **2**; that is, the chloride (Cl^-) also exists in the reaction mixture. However, no chloride is present in the resulted complex **2**; instead, CO_3^{2-} from hydration CO_2 was found in **2**.

Coordination polymers with specific structures have been obtained by reactions of metal salts with suitable organic ligands;[14−16] however, most of the reported infinite helices are Ag(I) and Cu(I) complexes with tetrahedral coordination preference of the metal ions and long flexible ligands.[14] For example, double-stranded helical structure was observed in complex $[Ag(bpp)](CF_3SO_3)$ [bpp = 1,3-bis(4-pyridyl)-propane], which was stabilized by weak Ag···Ag ($d^{10}-d^{10}$)

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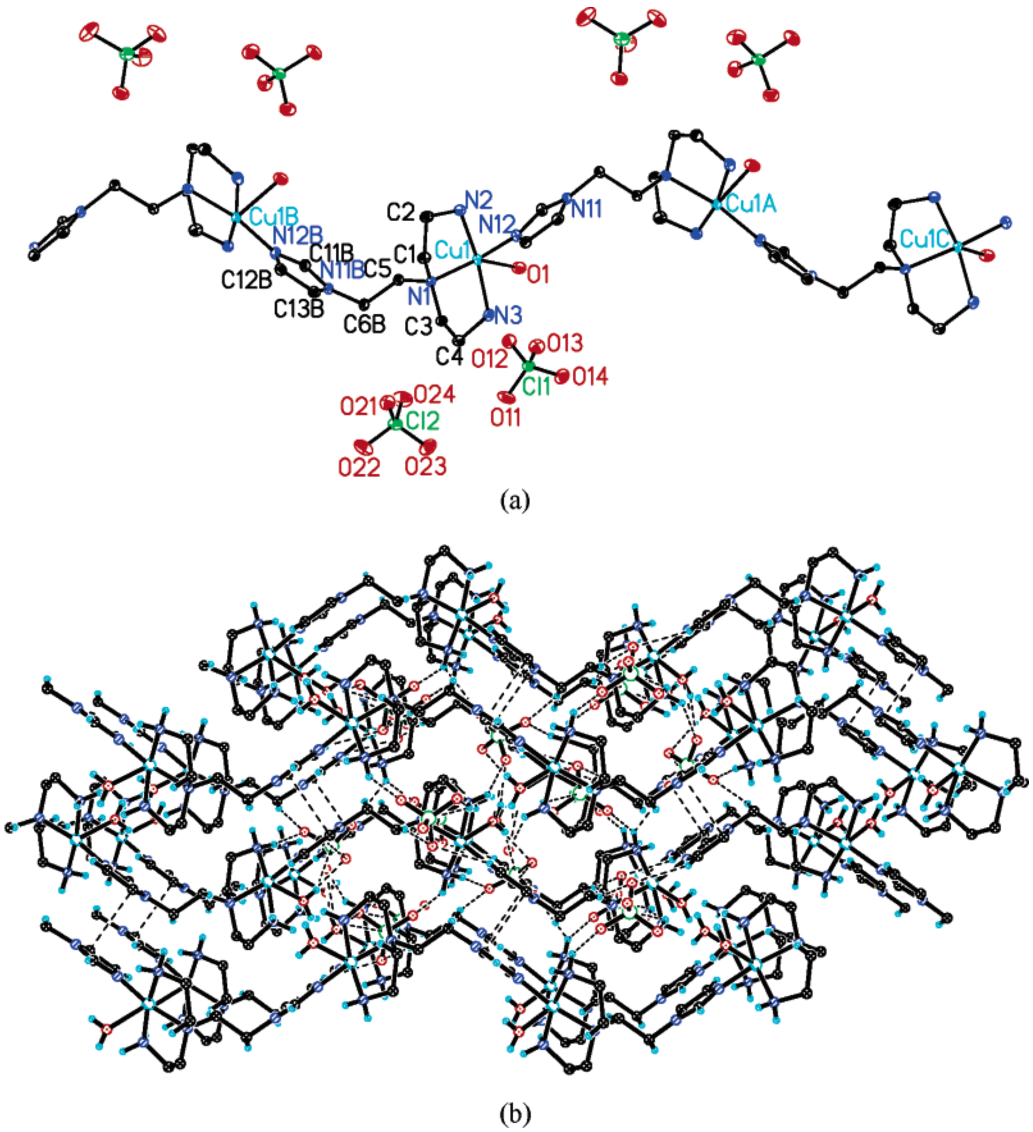
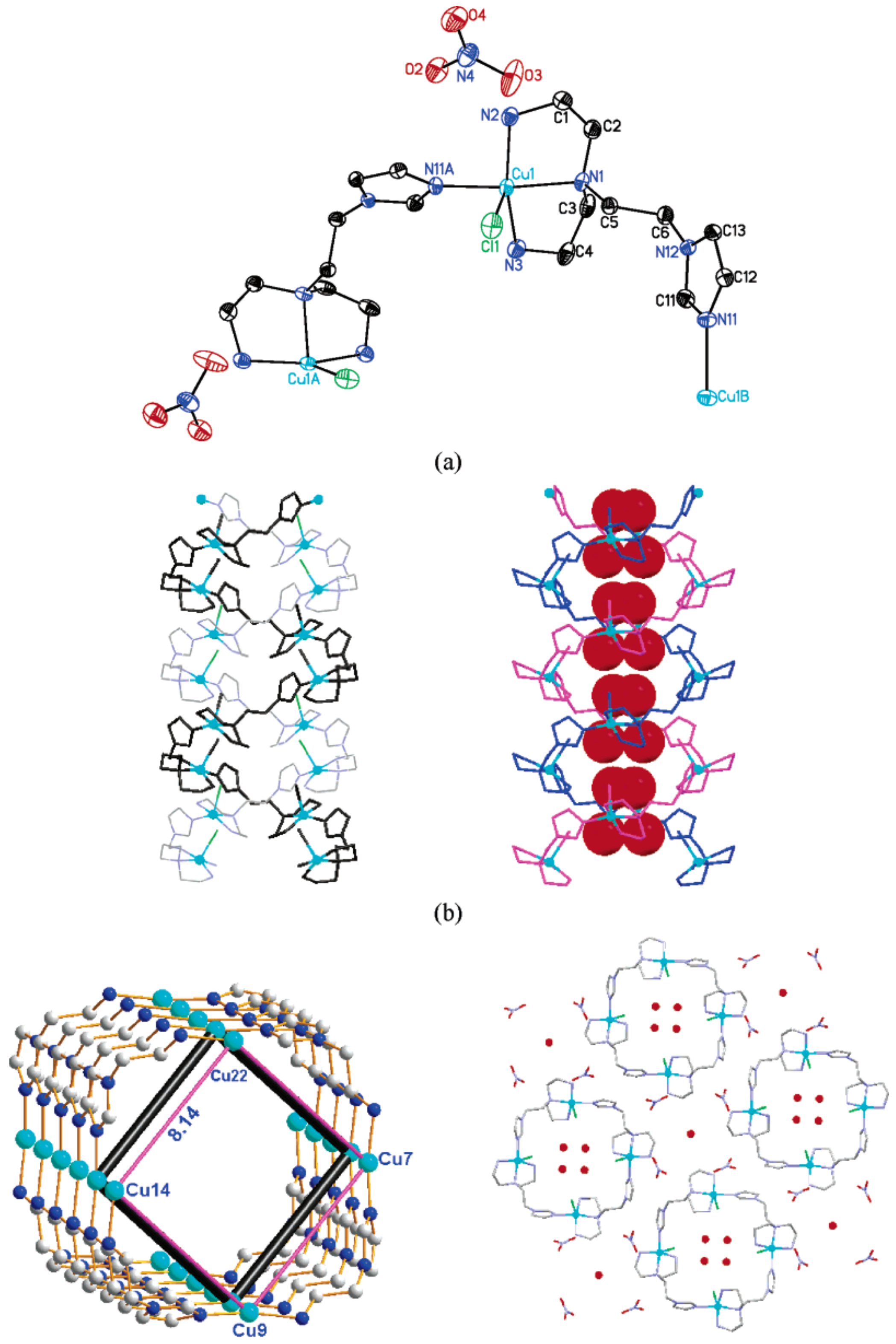


Figure 3. (a) 1D chain structure of **4** with atom numbering scheme (hydrogen atoms were omitted for clarity). (b) 3D network formed by hydrogen bonding indicated by the dashed line, packed along the *a* axis of **4**.

interactions with a Ag−Ag distance of 3.09 Å.[14a] An infinite double-stranded helix of **5** obtained by reaction of a tripodal polyamine ligand with an octahedral Cu(II) center has not been well-documented. Because the left- and right-stranded helical chains coexist in the structure, no chirality was detected for complex **5**. The occurrence of helical structure may be contributed to by the flexibility of the imidazolethyl pendant of L. Another remarkable feature of **5** is that the two infinite helices intertwine and generate a 1D rhombic channel with a large cavity filled by the lattice water molecules as shown in Figure 4b,c. As a simplified view shown in Figure 4c (left), the channel could be viewed as an extended rhombic array of four Cu(II) atoms in a plane with a dimensions of 8.14 × 8.14 Å (along each edge, e.g., Cu14−Cu22 and Cu22−Cu7) and 10.57 (Cu9−Cu22) and 12.39 (Cu7−Cu14) Å (along the diagonal). It should be noted that the N−H···O hydrogen bonds between the ligand L and water oxygen atom played an important role in holding the water molecules in the channel. Furthermore, the double-stranded helical chains of complex **5** are also stabilized by significant N−H···Cl and C−H···Cl hydrogen bonds between the ligand from one helical chain and one Cl^- anion (Cl1) from the other chain (Table 3 and Figure S1, Supporting Information). This implied that the coordination of Cl^- might also play an important role in the formation of the final helical structure because only a 1D zigzag chain structure was observed in complex **4** with a coordinated water molecule. In addition, the nitrate anions were located regularly between the chains and were held there by hydrogen bonds as show in Figure S1, Supporting Information.

Magnetic Property of Complex 2. The study of magnetic property of metal−carbonato complexes is of great interest due to the wide diversity of magnetic behaviors caused by versatile coordination modes of the carbonato ligand. Herein, the magnetic property of the μ_3-η^1:η^1:η^1-tridentate CO_3^{2-} coordinated Cu(II) complex **2** was investigated. The temperature dependence of the magnetic susceptibility of complex **2** is shown in Figure 5, and the observed $\chi_M T$ value at room temperature is 1.37 emu K mol^{-1}, which is larger



(a)

(b)

(c)

Figure 4. (a) ORTEP plot of structure of **5** with atom numbering scheme (hydrogen atoms were omitted for clarity). (b) The double-stranded helical chain generated by two intertwined single-stranded helical chains (left) and including water molecules inside the channel, which were shown in space-filling mode (right). (c) A simplified view of the rhombic array of four Cu(II) ions of the channel with Cl^- anions and the aminoethyl pendant of the ligand omitted for clarity (left) and the packing structure of the double-stranded helical chains along the *c* axis, including water molecules and nitrate anions (right).

than the expected value of 1.24 emu K mol^{-1} based on the spin-only Cu_3 unit ($S = 1/2$ and $g = 2.1$). As the temperature is lowered, $\chi_M T$ increases continuously to a maximum value of 2.09 emu K mol^{-1} at 7 K indicating that the ferromagnetic interaction between the Cu(II) ions by the bridging of CO_3^{2-} is the dominating magnetic property of **2**. When the tem-

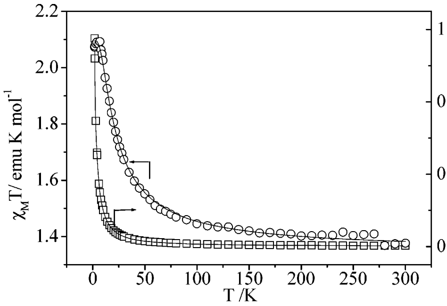


Figure 5. Plots of the temperature dependences of χ_M (□) and $\chi_M T$ (○) for complex **2**. Solid lines show the best fit obtained (see text).

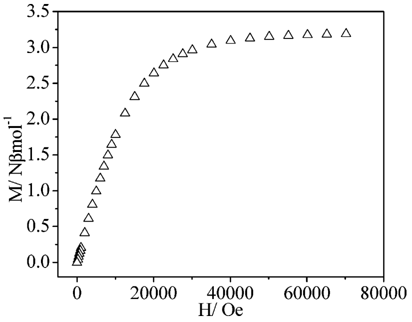


Figure 6. Magnetic field (H) dependence of M (Nβ mol^{-1}) for complex **2** at 1.8 K.

perature is below 7 K, $\chi_M T$ decreases to 2.07 emu K mol^{-1}, which may be caused by weak intercluster interactions at very low temperature. In the $M-H$ plot as shown in Figure 6, the magnetization varies linearly with low applied fields up to 2.25 T and then progressively tends to completely saturation with a value of 3.18 Nβ mol^{-1} when the field reaches 7 T, which is similar to the expected value of 3.15 Nβ mol^{-1} based on the spin-only Cu_3 unit ($S = 1/2$ and $g = 2.1$). Such behavior confirmed that the ferromagnetic coupling is dominating in **2**. No hysteresis loop was observed, suggesting that the magnetic phase critical temperature is probably lower than 1.8 K. Additional evidence is given in alternating current magnetic measurements (Figure S2, Supporting Information), where the magnetizations of both in- and out-of-phase increase with the decreasing temperature but no peaks were observed. On the basis of the μ_3-η^1:η^1:η^1-tridentate bridging mode of CO_3^{2-}, the magneto-structure of Cu(II) centers in **2** could be simplified as a trinuclear triangular array cluster as schematically shown in Scheme 3. So the experimental data were fitted to the expression derived from the Hamiltonian as eq 1:

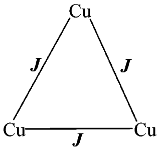
$$H = -J(S_1S_2 + S_1S_3 + S_2S_3) \qquad (1)$$

In addition, the expression of molar susceptibility derived from the Hamiltonian could be written as eq 2:[17,18a]

$$\chi_M = \chi'/[1 - (2zJ'\chi')/Ng^2\beta^2] \quad \text{and}$$
$$\chi' = [(Ng^2\beta^2)(1 + 5\exp(3J/2kT))]/[4kT(1 + \exp(3J/2kT))] \qquad (2)$$

J is donated as the exchange parameter between the conjoined Cu(II) ions through the CO_3^{2-}, and to fit the low-temperature data, a zJ' parameter is also defined allowing

Scheme 3



for intercluster exchange.[17] The fit was performed by minimizing the function $R = \sum[(\chi_M)_{calcd} - (\chi_M)_{obs}]^2/\sum(\chi_M)_{obs}{}^2$, the best fit giving parameters $J = 14.2$ cm^{-1}, $g = 2.12$, $zJ' = -0.0018$ cm^{-1}, and $R = 3.3 \times 10^{-7}$. The small J value revealed weak ferromagnetic interaction between the Cu(II) ions due to the large Cu−Cu separation of 4.87 Å in the trinuclear cluster (Scheme 3), which agreed well with the experimental result discussed above. In addition, such magnetic parameters are consistent with the previously reported carboanto-bridged trinuclear Cu(II) complexes, for example, $[(\mu_3\text{-}CO_3)Cu_3(dpt)_3](ClO_4)_4$ [dpt = bis(3-aminopropyl)amine] with $J = 15.8$ cm^{-1}, $g = 2.060$, $zJ' = -0.015$ cm^{-1},[5a,18] and $[\{(mpepma)Cu(OClO_3)\}_3(\mu_3\text{-}CO_3)]ClO_4$ [mpepma = methyl-[2-(2-pyridyl)ethyl](2-pyridylmethyl)amine] ($J = 18$ cm^{-1}, $g = 2.11$, $zJ' = -0.36$ cm^{-1}).[19] However, the magnetic property of **2** is different from that observed in complex $[(\mu_3\text{-}CO_3)(CuTPA)_3](ClO_4)_4$ [TPA = tris(pyridylmethyl)amine] which shows a very weak antiferromagnetic exchange coupling with $J = -1.19$ cm^{-1}, $g = 2.02$.[20]

TGA and XRPD Analysis. Structural analyses revealed that there are large cavities in complexes **1**, **2**, and **5**. In addition, the solvent molecules cover 13.5% (372 Å^3), 18.8% (524 Å^3), and 17.0% (560 Å^3) of the unit cell volumes of **1**, **2**, and **5**, respectively. It is important to investigate the stability of such complexes after removal of the clathrate molecules for developing potential porous materials. No TGA was carried out for **1** and **2** due to the potential explosibility of the perchlorate salt upon heating. The XPRD analyses were performed for **1** and **2** after drying the crystal samples at the room temperature for 2 h because the acetonitrile molecules in **1** and **2** are easy to lose (vide supra), and the loss of CH_3CN molecules was confirmed by the elemental analysis. It can be seen from Figures S3 and S4 (Supporting Information) that the framework structures of complexes **1** and **2** are retained after removal of guest molecules. The TGA and XPRD investigations were carried out for complex **5**. TGA data (Figure S5) revealed that an initial weight loss of 5.5% below 155 °C corresponds to the loss of 1.25 water molecules per $[Cu(L)Cl]NO_3{\cdot}1.25H_2O$ (calcd 5.9%). Unfortunately the XPRD data of complex **5** (Figure S6, Supporting Information) after the removal of water molecules by heating the sample of complex **5** under 155 °C for 2 h showed the loss of crystallinity. Thus the helices were not maintained

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in the absence of guest molecules in the cavities. No TGA and XPRD were investigated for complexes **3** and **4** due to the presence of perchlorate anions and no porosity of the complexes.

Conclusions

In our present and previous studies, an imidazole-containing tripodal polyamine ligand *N*^{1}-(2-aminoethyl)-*N*^{1}-(2-imidazolethyl)-ethane-1,2-diamine (L) was used to react with metal salts with different metal centers, with different counteranions, or under different reaction pH, and the results showed that the metal ions, counteranions, and reaction pH have great influence on the formation and the structure of the complexes. It was found that the absorption and hydration of atmospheric carbon dioxide to give carbonato complexes only occurred at alkaline pH 9 with perchlorate salts. A μ_3-η^2:η^2:η^2-tridentate bridging mode of CO_3^{2-} was found in Cd(II) complex $[Cd_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4 \cdot 2CH_3CN$ with 2D network structure, while in the Cu(II) complex $[Cu_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4 \cdot 3CH_3CN$, the CO_3^{2-} has a μ_3-η^1:η^1:η^1-tridentate bridging mode. The magnetic behavior of the μ_3-η^1:η^1:η^1-carbonato−Cu(II) complex was investigated over the temperature range 1.8−300 K, and weak ferromagnetic coupling was found in the trinuclear triangular Cu_3 array.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grant 20231020) and the National Science Fund for Distinguished Young Scholars (Grant 20425101).

Supporting Information Available: X-ray crystallographic file in CIF format and crystal packing diagram for complex **5** (Figure S1), the plot of the ac magnetic measurements (Figure S2), the XRPD diagrams for complexes **1** (Figure S3), **2** (Figure S4), and **5** (Figure S6), and TGA data of **5** (Figure S5). This material is available free of charge via Internet at http://pubs.acs.org.

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