

# Three-Dimensional Structure of Barium–Cupric Nitrilotriacetate and One-Dimensional Structure of Cobalt–Cupric Nitrilotriacetate: Template Effect of Cations on the Formation of Coordination Polymers

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**Abstract** Three mixed-metal nitrilotriacetates  $[\text{Ba}(\text{H}_2\text{O})_3\text{Co}(\text{nta})\text{Cl}]_n$  (**1**),  $[\text{Ba}(\text{H}_2\text{O})_3\text{Ni}(\text{nta})\text{Cl}]_n$  (**2**), and  $[\text{Ba}(\text{H}_2\text{O})_3\text{Cu}(\text{nta})\text{Cl}]_n$  (**3**) ( $\text{H}_3\text{nta}$  = nitrilotriacetic acid) were prepared by the reaction of  $\text{M}^{2+}$  ions ( $\text{M} = \text{Co}, \text{Ni}, \text{and Cu}$ ),  $\text{K}_3\text{nta}$ , and  $\text{Ba}^{2+}$  ions in water. The reaction of complexes **1** and **2** with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  afforded  $[\text{Co}(\text{H}_2\text{O})_6]_n[\text{Cu}_2(\text{nta})_2]_n \cdot 2n\text{H}_2\text{O}$  (**4**) and  $[\text{Ni}(\text{H}_2\text{O})_6]_n[\text{Cu}_2(\text{nta})_2]_n \cdot 2n\text{H}_2\text{O}$  (**5**), respectively. The reaction mechanism was elucidated. The crystal structure analyses indicate that the  $\text{Ba}^{2+}$  ions formed one-dimensional (1D) zigzag chains in complex **3**, and the chains were connected by  $\text{Cu}(\text{nta})^-$  anions to form a three-dimensional network. On the other hand, in complexes **4** and **5**, the  $\text{Cu}(\text{nta})^-$  anions formed 1D zigzag chains, and the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (or  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ) cations existed as isolated units.

**Keywords** Template effect · Nitrilotriacetate · Coordination polymer · Crystal structure

## 1 Introduction

In recent years, the use of suitable coordination complexes as the building blocks for the synthesis of oligomers or polymers has attracted much interest. Indeed, many materials obtained by self-assembly synthesis strategies exhibit novel structural topologies and/or suitable optical and/or magnetic properties [1–8]. Nitrilotriacetic acid ( $\text{H}_3\text{nta}$ ) is used as a complexing agent to form coordination polymers [9–13]. Many studies reported that protonated and deprotonated nitrilotriacetates afforded various Cu complexes, and the nitrilotriacetato ligand behaved as a tridentate or tetradentate chelate that binds through the amino N and carboxyl O atoms [14–19]. Among these complexes, several Cu atoms acted as tetradentate chelating agents instead of tridentate chelating agents in the formation of coordination polymer. Herein, we report new types of polymeric Cu nitrilotriacetate complexes  $[\text{Co}(\text{H}_2\text{O})_6]_n[\text{Cu}_2(\text{nta})_2]_n \cdot 2n\text{H}_2\text{O}$  (**4**) and  $[\text{Ni}(\text{H}_2\text{O})_6]_n[\text{Cu}_2(\text{nta})_2]_n \cdot 2n\text{H}_2\text{O}$  (**5**) using Co, Ni, and Cu nitrilotriacetate complexes ( $[\text{Ba}(\text{H}_2\text{O})_3\text{Co}(\text{nta})\text{Cl}]_n$  (**1**),  $[\text{Ba}(\text{H}_2\text{O})_3\text{Ni}(\text{nta})\text{Cl}]_n$  (**2**), and  $[\text{Ba}(\text{H}_2\text{O})_3\text{Cu}(\text{nta})\text{Cl}]_n$  (**3**)) as the starting materials. The template effect of the cations,  $\text{Ba}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ , on the structure of  $\text{Cu}(\text{nta})^-$  anions was investigated.

## 2 Experimental Section

### 2.1 Synthesis of $[\text{Ba}(\text{H}_2\text{O})_3\text{M}(\text{nta})\text{Cl}]_n$ (**1**, $\text{M} = \text{Co}$ ; **2**, $\text{M} = \text{Ni}$ ; **3**, $\text{M} = \text{Cu}$ )

Complex **1** was prepared by the reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (4.8 g, 20 mmol) with potassium nitrilotriacetate ( $\text{K}_3\text{nta}$ , 6.2 g, 20 mmol) in 50 mL water. Barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , 5.0 g, 20 mmol) was added and stirred for

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1.5 h and filtered. After several days of slow evaporation of the solvent at room temperature, violet solids obtained were collected, washed with water, and air-dried to afford 2.6 g (5.49 mmol) of product **1** (27.5 % yield). Anal. Calc for  $C_6H_{12}BaClCoNO_9$  (%): C, 15.19; H, 2.53; N, 2.95. Found: C, 15.32; H, 2.72; N, 3.04. IR (KBr,  $cm^{-1}$ ):  $\nu_{as}(COO^-)$  1,629<sub>s</sub>, 1,590<sub>s</sub>;  $\nu_s(COO^-)$  1,408<sub>m</sub>.

Complex **2** was prepared in a similar manner as complex **1** except using  $NiCl_2 \cdot 6H_2O$  instead of  $CoCl_2 \cdot 6H_2O$  (37.0 % yield, 3.50 g, 7.39 mmol). Anal. Calc for  $C_6H_{12}BaClNiNO_9$  (%): C, 15.19; H, 2.53; N, 2.95. Found: C, 15.13; H, 2.81; N, 3.06. IR (KBr,  $cm^{-1}$ ):  $\nu_{as}(COO^-)$  1,629<sub>s</sub>, 1,590<sub>s</sub>;  $\nu_s(COO^-)$  1,405<sub>m</sub>.

The crystals of compound **2** for X-ray analysis were not obtained.

Complex **3** was prepared in a similar manner as complex **1** except that  $CuCl_2 \cdot 2H_2O$  was used instead of  $CoCl_2 \cdot 6H_2O$  (48.9 % yield, 4.80 g, 9.78 mmol). Anal. Calc for  $C_6H_{12}BaClCuNO_9$  (%): C, 15.05; H, 2.51; N, 2.93. Found: C, 15.22; H, 2.58; N, 2.87. IR (KBr,  $cm^{-1}$ ):  $\nu_{as}(COO^-)$  1,631<sub>s</sub>, 1,590<sub>s</sub>;  $\nu_s(COO^-)$  1,407<sub>m</sub>.

## 2.2 Synthesis of $[M(H_2O)_6]_n[Cu_2(NTA)_2]_n \cdot 2nH_2O$ (**4**, $M = Co$ ; **5**, $M = Ni$ )

Complex **4** was prepared by the reaction of complex **1** (1.4 g, 3.0 mmol) with cupric sulfate pentahydrate ( $CuSO_4 \cdot 5H_2O$ , 0.75 g, 3.0 mmol) in 50 mL water. The mixture was stirred for 1 h, and the solution was filtered. The filtrate was concentrated through slow evaporation at room temperature for several days. The resulting blue solid was collected, washed with water, and air-dried to afford 0.51 g (0.72 mmol) of product **4** (48.1 % yield). Anal. Calc for  $C_{12}H_{28}CoCu_2N_2O_{20}$  (%): C, 20.39; H, 3.96; N, 3.96. Found: C, 20.19; H, 4.28; N, 4.05. IR (KBr,  $cm^{-1}$ ):  $\nu_{as}(COO^-)$  1,627<sub>s</sub>;  $\nu_s(COO^-)$  1,399<sub>m</sub>.

Complex **5** was prepared in a similar manner as complex **4** except that complex **2** was used instead of complex **1** (38.0 % yield, 0.41 g, 0.57 mmol). Anal. Calc for  $C_{12}H_{28}Cu_2N_2NiO_{20}$  (%): C, 20.39; H, 3.96; N, 3.96. Found: C, 20.17; H, 4.26; N, 3.98. IR (KBr,  $cm^{-1}$ ):  $\nu_{as}(COO^-)$  1,627<sub>s</sub>;  $\nu_s(COO^-)$  1,398<sub>m</sub>.

## 2.3 Physical Measurements

The infrared (IR) spectra were recorded using a Nicolet 360 FT-IR spectrometer. The elemental analyses were performed using an EA 1110 elemental analyzer.

## 2.4 X-ray Data Collection, Structure Solution, and Refinement

The structural analyses were performed using a Bruker Smart Apex CCD diffractometer with graphite

monochromate Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation at 298 K. The data were collected for Lorentz and Polarization effects. An absorption correction was applied using the SADABS program [20]. The structures were primarily solved by the WinGX program [21] and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all the nonhydrogen atoms with SHELXL-97 [22]. All the H atoms on carbons were placed in calculated positions and refined in the riding mode. All the H atoms on  $H_2O$  molecules were located from the difference Fourier maps and refined with the O–H bond lengths fixed at 0.85  $\text{\AA}$ . Summaries of crystallographic data for complexes **1**, **3**, **4** and **5** are listed in Table 1. Selected bond distances and bond angles are listed in Tables 2 and 3.

## 3 Results and Discussion

### 3.1 Synthesis

Complexes **1**, **2**, and **3** were directly synthesized by the reactions of  $CoCl_2$ ,  $NiCl_2$ , and  $CuCl_2$  with nitrilotriacetate, respectively, and further used as the reactants for the preparation of complexes **4** and **5**. The pH value, molar ratio of the reactants, and reaction temperature were not crucial in the formation of complexes **4** and **5**. Notably, strongly bonded monomeric nitrilotriacetato cobalt(II) or nickel anion was substituted by  $H_2O$  molecules to form a tetradentate cation, which was different from the nitrilotriacetato Cu(II) anion. This is attributed to the formation of polymeric Cu nitrilotriacetato anion and the affinity of  $Cu^{2+}$  ion to nta ligand [23, 24]. The coordination constants ( $K_a$ ) also show the same result ( $\lg K_{Co-nta} = 10.8$ ,  $\lg K_{Ni-nta} = 11.53$ , and  $\lg K_{Cu-nta} = 12.96$ ). The synthetic routes to complexes 1–5 are shown in Fig. 1.

### 3.2 Infrared Spectra

In the IR spectra of complexes **4** and **5**, the asymmetric stretching vibrations  $\nu_{as}(COO^-)$  appear at 1,627  $cm^{-1}$ , and the symmetric stretching vibrations  $\nu_s(COO^-)$  appear at 1,399  $cm^{-1}$  for the two complexes (Figure S1). These bands were shifted to lower wavenumber compared to those of the free nitrilotriacetato ligand. The additional bands in the range 750–540  $cm^{-1}$  can be attributed to the absorption of Cu–O or Cu–N (Tables 4, 5).

### 3.3 Description of Crystal Structures

The molecular structure of complex **3** is shown in Fig. 2. The nta ligand coordinated to Cu in a tetradentate manner through three carboxyl O atoms (O1, O3, and O5) and one N atom. The fifth coordination site of Cu was occupied by

**Table 1** Crystal data and structure refinement for **1**, **3**, **4** and **5**

Complex code	<b>1</b>	<b>3</b>	<b>4</b>	<b>5</b>
Empirical formula	C <sub>6</sub> H <sub>12</sub> NO <sub>9</sub> ClBaCo	C <sub>6</sub> H <sub>12</sub> NO <sub>9</sub> ClBaCu	C <sub>12</sub> H <sub>28</sub> N <sub>2</sub> O <sub>20</sub> CoCu <sub>2</sub>	C <sub>12</sub> H <sub>28</sub> N <sub>2</sub> O <sub>20</sub> NiCu <sub>2</sub>
Formula weight	473.89	478.50	706.37	706.15
Crystal color	Brown	Blue	Indigo	Blue
Crystal dimension (mm)	0.21 × 0.19 × 0.16	0.36 × 0.33 × 0.15	0.20 × 0.10 × 0.10	0.32 × 0.22 × 0.11
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
<i>a</i> /Å	9.0636(13)	9.1282(17)	12.646(3)	6.3535(15)
<i>b</i> /Å	17.244(3)	17.229(3)	11.234(2)	16.253(4)
<i>c</i> /Å	8.4396(13)	8.2621(16)	16.298(3)	11.271(3)
$\beta$ (°)	91.921(2)	91.151(4)	90	93.824(4)
<i>V</i> (Å <sup>3</sup> )	1,318.3(3)	1,299.1(4)	2,315.3(2)	1,161.3(5)
Space group	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> /c	P na2 <sub>1</sub>	P 2 <sub>1</sub>
<i>Z</i>	4	4	4	2
<i>D</i> <sub>calc</sub> (g cm <sup>−3</sup> )	2.388	2.446	2.026	2.020
<i>F</i> (000)	908	916	1,436	720
Reflections	9,215/2,301	7,259/2,266	15,645/4,065	5,596/3,392
Collected/unique/ <i>R</i> <sub>int</sub>	0.0217	0.0444	0.0284	0.1125
Data/restraints/parameters	2,301/2/180	2,266/7/190	4,065/1/351	3,392/1/340
$\theta$ range (°)	2.25–24.99	2.23–25.00	2.20–25.00	2.20–25.00
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.868	1.037	1.186	1.519
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0243, 0.0927	0.0255, 0.0636	0.0275, 0.0711	0.0796, 0.1950

**Table 2** Selected bond distances (Å) and bond angles (°) for complex **1**

Co–O(1)	2.010(2)	Co–N	2.165(3)
Co–O(3)	1.965(2)	Co–Cl	2.3223(10)
Co–O(5)	1.981(3)	Ba–O(1)	3.012(2)
Ba–O(2)#3	2.749(3)	Ba–O(2)	2.853(3)
Ba–O(6)#2	2.739(3)	Ba–O(6)#4	2.897(3)
Ba–O(4)#1	2.712(3)	Ba–O(91)	2.810(3)
Ba–O(93)	2.778(3)	Ba–O(5)#4	2.986(3)
Ba–O(92)	2.929(4)		
O(1)–Co–O(3)	114.32(12)	O(3)–Co–N	80.30(10)
O(1)–Co–O(5)	118.22(11)	O(3)–Co–Cl	102.39(8)
O(1)–Co–N	79.87(10)	O(5)–Co–N	80.25(10)
O(1)–Co–Cl	98.06(7)	O(5)–Co–Cl	99.11(8)
O(3)–Co–O(5)	118.85(12)	N–Co–Cl	177.14(7)

Symmetry transformations used to generate equivalent atoms

#1  $-x, -y, -z + 1$ ; #2  $x + 1, -y + 1/2, z - 1/2$ ; #3  $x, -y + 1/2, z - 1/2$ ; #4  $x + 1, y, z$ ; #5  $x, -y + 1/2, z + 1/2$ #6  $x - 1, -y + 1/2, z + 1/2$ ; #7  $x - 1, y, z$ 

a Cl<sup>−</sup> ion, forming a distorted trigonal bipyramidal coordination polyhedron around Cu (Fig. 2a). The Cu–O bond lengths [Cu–O(1), 1.970(3) Å; Cu–O(3), 1.976(3) Å; and Cu–O(5), 2.090(2) Å] and Cu–N bond length [1.999(3) Å] are slightly shorter than the Cu–Cl bond length

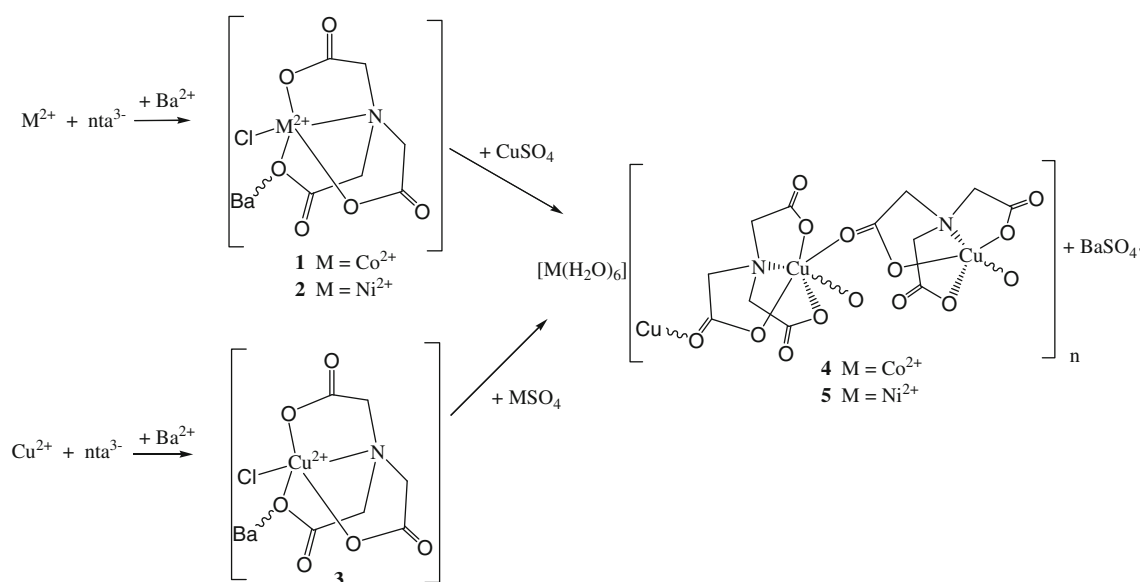
**Table 3** Selected bond distances (Å) and bond angles (°) for complex **3**

Cu–O(1)	1.970(3)	Cu–N	1.999(3)
Cu–O(3)	1.976(3)	Cu–Cl	2.2327(10)
Cu–O(5)	2.090(2)	Ba···Ba#2	4.598(3)
Ba–O(2)#1	2.701(3)	Ba–O(6)	2.842(3)
Ba–O(6)#2	2.718(3)	Ba–O(4)#4	2.877(3)
Ba–O(4)#3	2.723(3)	Ba–O(91)	2.925(3)
Ba–O(93)	2.784(3)	Ba–O(5)	2.928(3)
Ba–O(92)	2.790(3)	Ba–O(3)#4	3.032(3)
O(1)–Cu–O(3)	126.90(14)	O(3)–Cu–N	83.64(11)
O(1)–Cu–O(5)	127.1(2)	O(3)–Cu–Cl	96.53(8)
O(1)–Cu–N	83.90(11)	O(5)–Cu–N	81.17(10)
O(1)–Cu–Cl	98.64(9)	O(5)–Cu–Cl	95.82(7)
O(3)–Cu–O(5)	119.17(12)	N–Cu–Cl	176.60(8)

Symmetry transformations used to generate equivalent atoms

#1  $-x+1, -y, -z+1$ ; #2  $x, -y+1/2, z + 1/2$ ; #3  $x-1, -y+1/2, z + 1/2$ ; #4  $x - 1, y, z$ 

[2.2327(10) Å]. The Ba<sup>2+</sup> ion was ten-coordinated with three H<sub>2</sub>O molecules, two chelating nta carboxylate O atoms (O5 and O6), and five O atoms from symmetry-related carboxylate of other nta ligands. The Ba<sup>2+</sup> ions are bridged by two carboxyl O atoms (O4 and O6) of the nta ligand with a Ba–Ba distance of 4.598(3) Å, forming one-



**Fig. 1** Synthesis route of complexes 1–5

**Table 4** Selected bond distances (Å) and angles (°) for **4**

Cu(1)–O(2)	1.982(3)	Cu(2)–O(6a)	1.937(3)
Cu(1)–O(4)	1.974(2)	Cu(2)–O(7a)	2.381(3)
Cu(1)–O(5a)	2.406(3)	Cu(2)–O(8)	2.347(3)
Cu(1)–O(6)	2.329(3)	Cu(2)–O(10)	1.965(3)
Cu(1)–O(8)	1.937(3)	Cu(2)–O(12)	1.960(2)
Cu(1)–N(1)	2.027(3)	Cu(2)–N(2)	2.011(3)
O(2)–Cu(1)–O(4)	164.63(13)	O(6a)–Cu(2)–N(2)	173.87(13)
O(5a)–Cu(1)–O(6)	170.30(10)	O(7a)–Cu(2)–O(8)	169.43(11)
O(8)–Cu(1)–N(1)	173.29(13)	O(10)–Cu(2)–O(12)	165.30(13)

Symmetry code:  $A x + 1/2, -y + 1/2, z$

**Table 5** Selected bond distances (Å) and angles (°) for **5**

Cu(1)–O(2)	1.971(7)	Cu(2)–O(6a)	1.930(7)
Cu(1)–O(4)	1.957(7)	Cu(2)–O(7a)	2.382(8)
Cu(1)–O(5a)	2.433(10)	Cu(2)–O(8)	2.334(7)
Cu(1)–O(6)	2.362(7)	Cu(2)–O(10)	1.973(7)
Cu(1)–O(8)	1.923(7)	Cu(2)–O(12)	1.974(7)
Cu(1)–N(1)	2.025(8)	Cu(2)–N(2)	2.020(8)
O(2)–Cu(1)–O(4)	166.0(3)	O(6a)–Cu(2)–N(2)	173.6(3)
O(5a)–Cu(1)–O(6)	167.5(3)	O(7a)–Cu(2)–O(8)	168.6(3)
O(8)–Cu(1)–N(1)	172.5(3)	O(10)–Cu(2)–O(12)	164.9(4)

Symmetry code:  $A x + 1/2, -y + 1/2, z$

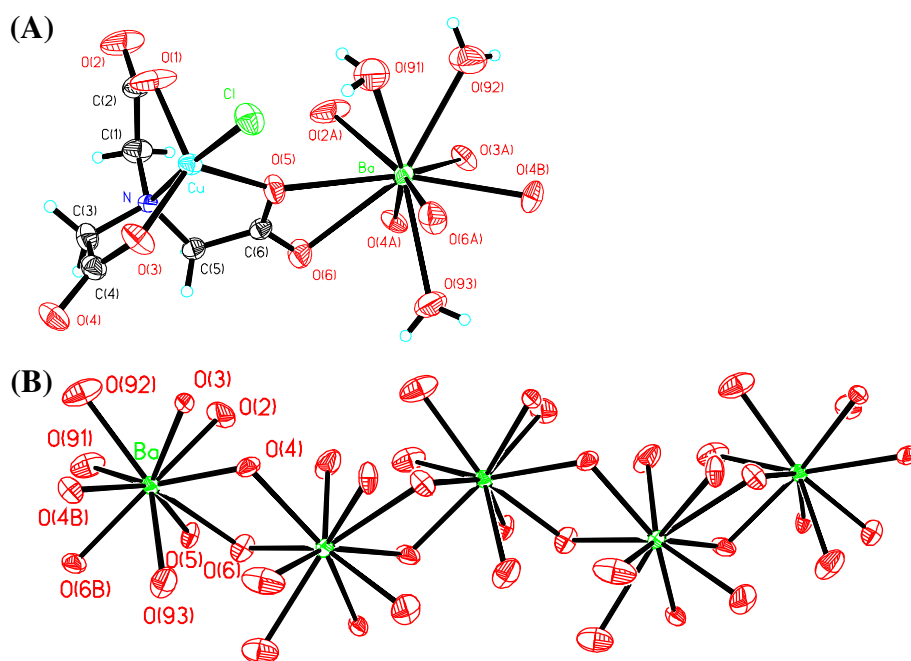
dimensional (1D) zigzag chains along the  $c$  axis (Fig. 2b). The barium chains were further connected by the  $CuCl(NTA)^{2-}$  anions to form a three-dimensional (3D) network (Fig. 3). Complex 3 is different from complex  $[La-CuCl(NTA)(H_2O)_6]ClO_4 \cdot H_2O$  [25], where the  $[Cu(NTA)Cl]^{2+}$  units are linked to each other by  $La(H_2O)_6^{3+}$  bridges in three

different directions, forming a two-dimensional (2D) metal-apex honeycomb, and for  $[Cu(Cl)(NTA)Sm(H_2O)_6] \cdot (ClO_4) \cdot (H_2O)$  [26], the two  $[Cu(NTA)Cl]^{2+}$  units are linked to each other by  $Sm(H_2O)_6^{3+}$  to form a 1D polymer. Complex 1 is an allomer of 3; the molecular and crystal structures of complex 1 are shown in the Supplementary Information (Figure S2).

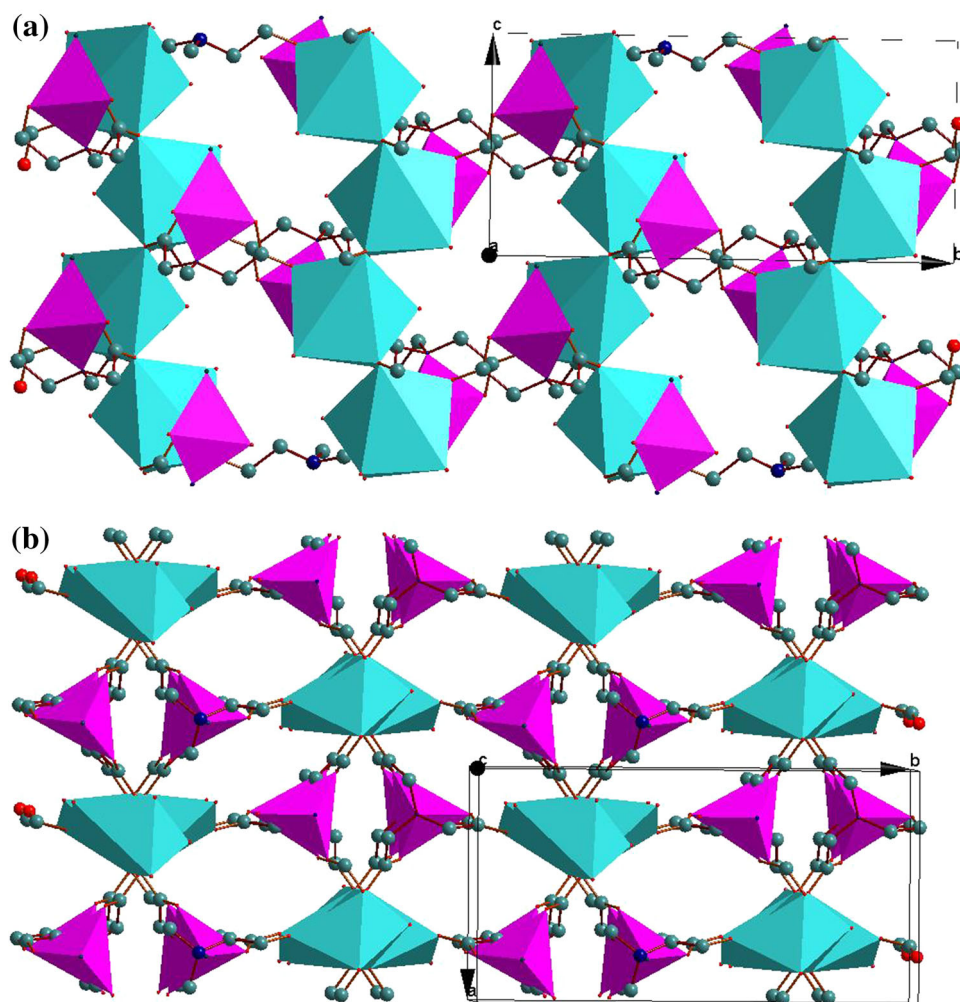
In complex 4, each asymmetric unit contains two  $Cu^{2+}$  ions, both of which lie in the center of a coordination octahedron (Fig. 4). Each coordination octahedron was obtained from one N atom and three carboxyl O atoms from one nta ligand and two carboxyl O atoms from two adjacent nta ligands. Bridged by the carboxyl O atoms (O6 and O8), the coordination octahedrons are linked to 1D zigzag chain in a share-apex mode (Fig. 5). In the octahedral geometry, the axial bonds of the  $Cu^{2+}$  ions were weakened by the Jahn–Teller distortion. Therefore, the two axial Cu–O bond lengths (2.329 and 2.406 Å) are clearly longer than the four equatorial Cu–O and Cu–N bond lengths in the range from 1.937 to 2.027 Å (Table 6).

The coordination geometry around Co in the  $[Co(H_2O)_6]^{2+}$  cation is also a distorted octahedron. The six Co–O bond lengths were 2.053(3), 2.088(2), 2.065(3), 2.085(3), 2.090(3), and 2.044(3) Å, respectively. An investigation of the crystal structure database (CSD) revealed that in the  $[Cu(H_2O)_6]^{2+}$  cation, four of the Cu–O bond lengths are short ( $\sim 1.97$  Å) and two Cu–O bond lengths are long ( $\sim 2.34$  Å); the M–O bond lengths of the hexahydrated cation in complex 4 indicate that the  $[M(H_2O)_6]^{2+}$  cation is  $[Co(H_2O)_6]^{2+}$  rather than  $[Cu(H_2O)_6]^{2+}$ . The result indicates that the  $Co^{2+}$  ions of  $Co(NTA)Cl^-$  unit in complex 1 have been replaced by  $Cu^{2+}$  ions, forming the  $Cu(NTA)^-$  anion and  $[Co(H_2O)_6]^{2+}$  cation in complex 4.

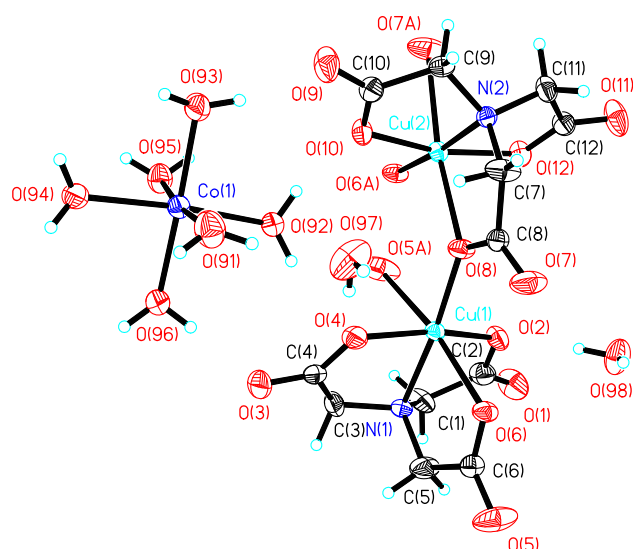
**Fig. 2** **a** Molecular structure of  $[\text{Ba}(\text{H}_2\text{O})_3\text{Cu}(\text{nta})\text{Cl}]_n$  (**3**) drawn at 50 % probability level; **b** A 1-D zigzag chain formed by the barium ions and oxygen atoms



**Fig. 3** The 3-D network of **3** viewed along axis *a* (**a**) and axis *c* (**b**). Cyanic polyhedrons, coordination polyhedrons around barium ions; pink octahedrons, coordination polyhedrons around cobaltic ions (Color figure online)







**Fig. 4** The molecular structure of complex **4** showing the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cation and the  $[\text{Cu}_2(\text{nta})_2]_n^{2n-}$  anion. Symmetry code: A '0.5 + x, 0.5 - y, z'

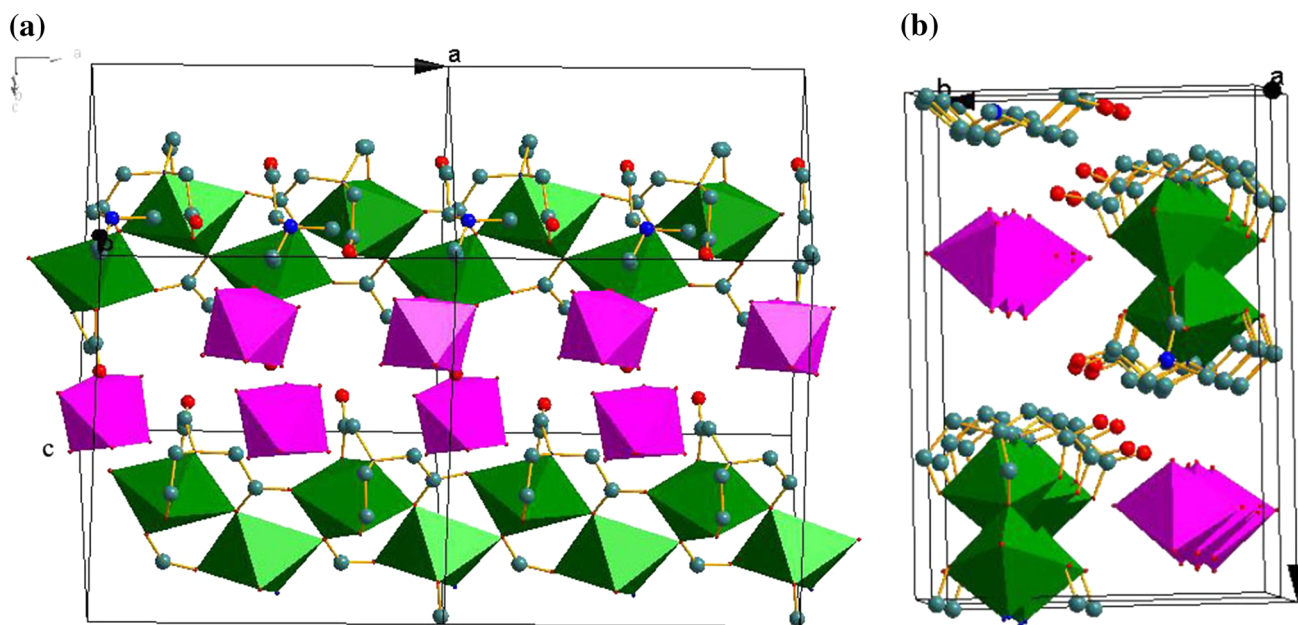
The structural difference in complex **3** and **4** may be caused by the difference in ion radius and maximum coordination number between barium and cobalt cations. With larger ion radius, the barium ions have a maximum coordination number of ten, which makes it be coordinated by the carboxyl O atoms from nta ligands besides the water molecules. On the other hand, with a much smaller ion radius, the cobalt ions have a maximum coordination

number of six which makes it be coordinated by six water molecules and forming a stable coordination octahedron. As a result, the cobalt ions were not coordinated by the carboxyl O atoms from nta ligands, which make it to be presented as isolated hydrated ions.

The coordinated  $\text{H}_2\text{O}$  O atom (O91) is H-bonded to two adjacent  $\text{H}_2\text{O}$  molecules  $[\text{O}(91)-\text{H}(91\text{A})\cdots\text{O}(97)$ , 2.753(5) Å and  $\text{O}(91)-\text{H}(91\text{B})\cdots\text{O}(98)$ , 2.687(4) Å], which are further H-bonded to two nta ligands. Another  $\text{H}_2\text{O}$  molecule (O95), which is H-bonded to O98  $[\text{O}(95)-\text{H}(95\text{B})\cdots\text{O}(98)$ , 2.771(4) Å], also formed a H-bond with two other nta ligands. Four parallel  $[\text{Cu}_2(\text{nta})_2]_n^{2n-}$  1D chains were linked together by  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  through H bonds, forming a quasi-3D structure. The  $\text{H}_2\text{O}$  molecules played important roles in the integrity of this structure because they were present in the structures of  $\text{K}[\text{Co}(\text{C}_6\text{H}_6\text{NO}_6)(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  [27] and  $\text{K}[\text{Cu}(\text{C}_6\text{H}_6\text{NO}_6)(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  [28]. The molecular structure of complex **5** was similar to that of **4** and is shown in the Supplementary Information (Figure S3).

### 3.4 Description of Thermal Stability

To examine the thermal stability of the title complexes, thermogravimetric analysis (TG) were carried out in the range of 20–800 °C (Fig. 6). For complex **1**, the first weight loss of 11.2 % from 60 to 110 °C (peak: 110 °C) corresponds to the loss of three coordinated water molecules of  $\text{Ba}^{2+}$  ion (calculated, 11.4 %). The remaining substance does not lose weight below 400 °C (peaks:

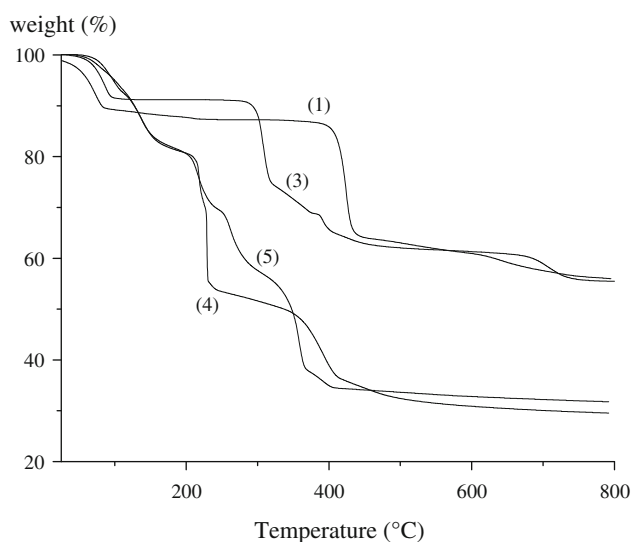


**Fig. 5** Polymeric structure of **4** viewed along axis *b* (a) and axis *a* (b) formed by the cupric nitrilotriacetate anions. Green octahedrons, coordination polyhedrons around cupric ions; pink octahedrons,

coordination polyhedrons around cobaltic ions. The non-coordinated water molecules were omitted for clarity (Color figure online)

**Table 6** Hydrogen bond distances (Å) and angles (°) for complex **4**

D—H—A	d (D—H)	d (H—A)	d (D—A)	∠(DHA)
O(91)—H(91A)···O(97)	0.85	1.92	2.753(5)	170
O(91)—H(91B)···O(98) i	0.85	1.87	2.687(4)	161
O(92)—H(92A)···O(4)	0.85	2.07	2.897(4)	166
O(92)—H(92B)···O(10)	0.85	1.84	2.673(4)	167
O(93)—H(93A)···O(9)	0.85	1.90	2.715(4)	162
O(93)—H(93B)···O(11) i	0.85	1.89	2.694(4)	157
O(94)—H(94A)···O(12) i	0.84	1.83	2.647(4)	165
O(94)—H(94B)···O(2) i	0.84	2.00	2.843(4)	178
O(95)—H(95A)···O(3) x	0.84	2.06	2.841(4)	154
O(95)—H(95B)···O(98) iii	0.85	1.98	2.771(4)	155
O(96)—H(96A)···O(1) i	0.84	1.86	2.671(4)	164
O(96)—H(96B)···O(3)	0.84	1.87	2.698(4)	171
O(97)—H(97A)···O(11) ii	0.85	2.37	3.181(5)	160
O(97)—H(97B)···O(4)	0.85	2.04	2.857(4)	163
O(98)—H(98A)···O(2)	0.84	1.86	2.703(4)	172
O(98)—H(98B)···O(10) ii	0.73	2.09	2.803(4)	168
C(1)—H(1B)···O(97) iv	0.97	2.58	3.335(5)	135
C(3)—H(3B)···O(9) ix	0.97	2.60	3.550(5)	167
C(5)—H(5A)···O(9) iv	0.97	2.39	3.286(6)	154
C(5)—H(5B)···O(11) v	0.97	2.55	3.466(6)	157
C(7)—H(7A)···O(1) vi	0.93	2.55	3.325(5)	141
C(9)—H(9A)···O(7) iii	0.97	2.60	3.050(5)	109
C(11)—H(11A)···O(3) vii	0.97	2.55	3.498(5)	167
C(11)—H(11B)···O(96) viii	0.97	2.57	3.414(5)	146

**Fig. 6** The thermal stability of complexes **1**, **3**, **4** and **5**

440 °C), after that the nitrilotriacetic acid ligand began to decompose. Finally,  $\text{BaCO}_3 \cdot \text{CoCO}_3$  was obtained (residual mass: observed, 64.3 %; calcd 65.6 %). The TG result of complex **3** was similar to that of complex **1**.

For complex **4**, the first weight loss of 15.8 % from 80 to 165 °C (peak: 160 °C) corresponds to the loss of six coordinated water molecules of  $\text{Co}^{2+}$  ion (calculated: 15.3 %). In 190–420 °C region (peak: 380 °C), the nitrilotriacetic acid ligands began to decompose when the temperature raise up. Finally,  $\text{CuCO}_3 \cdot \text{CoCO}_3$  was obtained (residual mass: observed, 34.9 %; calcd, 34.1 %). The TG results complex **5** was similar to that of complex **4**.

Through thermal decomposition of mixed-metal nitrilotriacetate coordination polymers,  $\text{BaCO}_3 \cdot \text{CoCO}_3$ ,  $\text{CuCO}_3 \cdot \text{CoCO}_3$  or  $\text{CuCO}_3 \cdot \text{NiCO}_3$  were obtained. The TG results here proposed a method for the preparation of binary mixed-metal carbonate.

## 4 Conclusions

Mixed-metal nitrilotriacetate coordination polymers,  $\text{M}-\text{Cu}(\text{nta})$ , were synthesized. The cations exhibited template effect on the structure of the anions,  $\text{Cu}(\text{nta})^-$ .

1. When the cation was  $\text{Ba}^{2+}$ , the  $\text{Cu}^{2+}$  ions were five-coordinated with trigonal bipyramid geometry. The hydrated  $\text{Ba}^{2+}$  ions formed 1D zigzag chains, and the chains were connected by the  $\text{Cu}(\text{nta})^-$  ions to form a 3D network.
2. When the cations were  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$ , the  $\text{Cu}^{2+}$  ions were six-coordinated with octahedron geometry, and  $\text{Cu}(\text{nta})^-$  ions were linked to a 1D zigzag chain. The  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  (or  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ) cations were present as isolated units.

The results here indicate that the radius and maximum coordination number of cations are important factor for the structure of coordination polymers. Our research work may give some insight into the design of coordination polymers and metal–organic frameworks (MOFs).

## 5 Supporting Information

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC). The assignment of CCDC codes are no. 979211–979214 for complex **1**, **3**, **4** and **5**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; E-mail address: deposit@ccdc.cam.ac.uk).

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