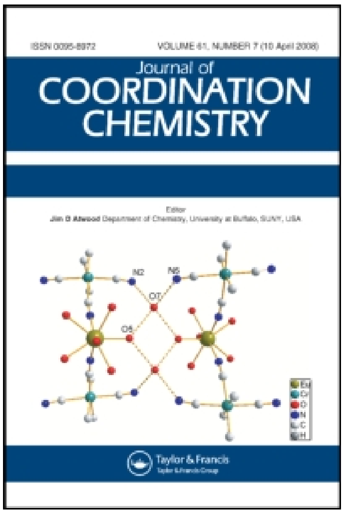

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Two cobalt coordination polymers with a highly undulated 2-D network and a 2-D (4,4) network

Li-Ming Zhu[a]; Hong-Liang Wang[a]; De-Yun Yuan[a]; Bao-Long Li[a]; Hai-Yan Li[a]
[a] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering and Material Science, Soochow University, Suzhou 215123, P.R. China

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Two cobalt coordination polymers with a highly undulated 2-D network and a 2-D (4,4) network

LI-MING ZHU, HONG-LIANG WANG, DE-YUN YUAN,
BAO-LONG LI* and HAI-YAN LI

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry
and Chemical Engineering and Material Science, Soochow University,
Suzhou 215123, P.R. China

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Two cobalt(II) coordination polymers [Co$_3$(ttmb)$_2$(H$_2$O)$_6$Cl$_6$]$\cdot$3H$_2$O (**1**) and Co(ttmb)$_2$(H$_2$O)$_2$](NO$_3$)$_2\cdot$4H$_2$O (**2**) were synthesized by the reaction of 1,3,5-tri(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene (ttmb) and CoCl$_2$ or Co(NO$_3$)$_2$. In **1**, each ttmb shows a tri-monodentate coordination mode and bonds three Co(II)s to form a highly undulated 2-D network. The Schläfla symbol for the 2-D network is 3^26^2. The highly undulated 2-D networks are not catenated, but interdigitate each other. In **2**, each ttmb shows a two-monodentate coordination mode and connects two Co(II)s to extend a 2-D (4,4) network. The ttmb exhibits the *cis,cis,cis*-conformation in **1** and the *cis,trans,trans*-conformation in **2**. The thermal stability of **1** was studied.

Keywords: Undulated network; Coordination polymer; 2-D network; 1,3,5-Tri(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene; Cobalt complex

1. Introduction

Design and synthesis of metal–organic frameworks have been intensely studied for applications as functional materials in selective guest adsorption, gas storage, ion exchange, nanoporous materials, and magnetic materials as well as a variety of architectures and topologies [1]. Flexible ligands have been used in recent years to obtain topologies not available from logical combinations of rigid building blocks. The simplest way to introduce flexibility into a ligand is by incorporating an alkyl chain into the spacer groups [2].

The ligands 1,2,4-triazole and its derivatives are very interesting because they combine coordination geometry of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms [3]. Our synthetic approach starts by focusing on the construction of new topological frameworks using flexible ligands by adjusting lengths and flexibilities such as 1,2-bis(1,2,4-triazol-1-yl)ethane [4], 1,4-bis(1,2,4-triazol-1-yl)butane [5], and 1,4-bis(1,2,4-triazol-1-ylmethyl) benzene [6].

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*Corresponding author. Email: libaolong@suda.edu.cn

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1,3,5-Tri(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene (scheme 1; ttmb) contains three triazole rings and can construct interesting coordination polymers. The anions play a key role in the construction of the coordination polymers [7]. In order to explore the influence on the structure of the inorganic anions, in this study, we synthesized two cobalt(II) coordination polymers $[Co_3(ttmb)_2(H_2O)_6Cl_6] \cdot 3H_2O$ (**1**) and $[Co(ttmb)_2(H_2O)_2](NO_3)_2 \cdot 4H_2O$ (**2**) by the reaction of the flexible ligand ttmb and $CoCl_2$ or $Co(NO_3)_2$.

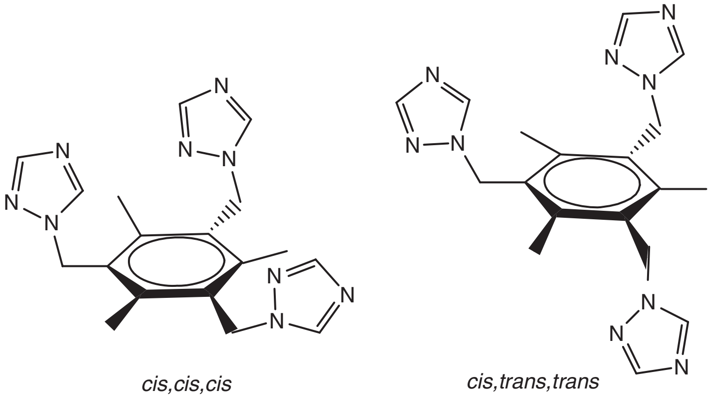
2. Experimental

2.1. *General procedures*

2.1.1. Materials and general methods. All reagents were of analytical grade and used without purification. The ligand ttmb was synthesized according to the method given in the literature [8]. Elemental analyses for C, H, and N were performed on a Perkin Elmer 240C analyser. Infrared (IR) spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer from 4000 to 400 cm^{-1}. Thermogravimetric analysis (TGA) was measured on a Thermal Analyst 2100 TA Instrument and SDT 2960 Simultaneous TGA-DTA Instrument in flowing dinitrogen at a heating rate 10°C min^{-1}.

2.2. *Synthesis of $[Co_3(ttmb)_2(H_2O)_6Cl_6] \cdot 3H_2O$ (1)*

First, $CoCl_2 \cdot 6H_2O$ (0.180 g, 0.75 mmol) aqueous solution (10 mL) was taken in a tube, and ttmb (0.182 g, 0.5 mmol) C_2H_5OH solution (10 mL) was slowly added to it. Pink crystals of **1** (0.158 g, yield: 58%) were obtained after about 2 weeks. Anal. Calcd for $C_{36}H_{60}Cl_6Co_3N_{18}O_9$ (**1**) (%): C, 33.82; H, 4.73; and N, 19.72. Found (%): C, 33.65; H, 4.62; and N, 19.57. IR data (cm^{-1}): 3379 vs, 3240 s, 3125 s, 1651 s, 1535 s, 1504 w, 1342 m, 1288 s, 1211 m, 1134 s, 1026 m, 995 m, 902 m, 825 w, 710 w, 679 s, 532 w, and 440 w.



Scheme 1. Two conformations of ttmb.

2.3. *Synthesis of* $[Co(ttmb)_2(H_2O)_2](NO_3)_2 \cdot 4H_2O$ *(2)*

The synthetic procedure of **2** was similar to **1**, except that $Co(NO_3)_2 \cdot 6H_2O$ (0.146 g, 0.50 mmol) was used instead of $CoCl_2 \cdot 6H_2O$. Red crystals of **2** (0.135 g, yield: 53% based on ttmb) were obtained after about 2 weeks. Anal. Calcd for $C_{36}H_{54}CoN_{20}O_{12}$ (**2**) (%): C, 42.48; H, 5.35; and N, 27.53. Found (%): C, 42.43; H, 5.31; and N, 27.42. IR data (cm^{-1}): 3460 s, 3348 s, 3109 s, 1651 w, 1573 w, 1531 m, 1385 vs, 1335 s, 1281 s, 1211 m, 1134 s, 1015 m, 991 m, 968 w, 895 w, 829 w, 783 w, 679 m, and 644 w.

2.4. *X-ray crystallography*

For X-ray crystallography studies, suitable single crystals of **1** and **2** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Rigaku Mercury charge-coupled device (CCD) diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensities were collected by the ω-scan technique. Structures were solved by direct methods and refined with a full-matrix least-squares technique (*SHELXTL-97*) [9]. The positions of hydrogens in ttmb were determined with theoretical calculation. Hydrogens in coordination water were located from successive Fourier syntheses. No hydrogens of disordered lattice waters were found. The parameters of the crystal data collection and refinement of **1** and **2** are given in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure*

The crystal structure of **1** shows that each cobalt(II) displays a distorted octahedral coordination geometry, coordinated by two triazole nitrogens (Co(1)–N(3), 2.125(4) Å) from two ttmb ligands and two oxygens from water (Co(1)–O(1), 2.102(4) Å) in an equatorial plane, and two Cl^- (Co(1)–Cl(1), 2.4882(13) Å) in the axial positions (figure 1). The Co–N and Co–O bond lengths are within normal values, but the Co–Cl bond lengths are longer than normal. Each ttmb shows *cis,cis,cis*-conformation as tri-monodentate linking three different cobalt(II)s. Each cobalt(II) connects four other cobalt(II)s to form a 2-D network (figure 2). The Schläfla symbol for the 2-D network is 3^26^2. The Co $\cdots$ Co distance separation by ttmb is 7.192(1) Å.

The 2-D network of **1** is highly undulated with a total thickness of 11.2 Å (figure 3). In order to minimize the big void cavities and stabilize the framework, the potential voids formed by a single 2-D network show incorporation of two other identical networks. The highly undulated 2-D networks are not catenated, but just interdigitate (figures 4 and 5).

Many undulated 2-D networks have been synthesized. Most of them are simply stacked [5b, 10]. $\{[Co(bte)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O\}_n$ (bte = 1,4-bis(1,2,4-triazol-1-yl)ethane) [4b] and $\{[Zn(btb)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O\}_n$ (btb = 1,4-bis(1,2,4-triazol-1-yl)butane) [5b] have undulated 2-D (4,4) network. In the superposition structure, the 2-D networks are stacked in an offset fashion so that the convex of one network can project into the concave of the other network. $[Co(him)(bdc)]_n$ (him = 1,1′-(1,4-hexanediyl)

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{36}H_{60}Cl_6Co_3N_{18}O_9$	$C_{36}H_{54}CoN_{20}O_{12}$
Formula weight	1278.51	1017.92
Temperature (K)	293(2)	223(2)
Crystal system	Trigonal	Monoclinic
Space group	*R-3*	*P 2(1)/n*
Unit cell dimensions (Å, °)		
a	14.384(2)	8.437(1)
b	14.384(2)	16.361(2)
c	21.678(4)	17.503(2)
α	90	90
β	90	101.113(3)
γ	120	90
Volume (Å^3), Z	3884.5(11), 3	2370.9(5), 2
Calculated density (g cm^{-3})	1.640	1.426
Absorption coefficient (mm^{-1})	1.328	0.442
$F(000)$	1971	1066
Reflections collected	12,654	13,511
Independent reflections	1580 [R(int) = 0.0612]	5333 [R(int) = 0.0476]
Goodness-of-fit on F^2	1.067	1.081
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0617$, $wR_2 = 0.1689$	$R_1 = 0.0799$, $wR_2 = 0.2076$
Parameters	120	328

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Co(1)–N(3)	2.125(4)	Co(1)–O(1)	2.102(4)
Co(1)–Cl(1)	2.4882(13)		
N(3)–Co(1)–N(3A)	180.0(3)	N(3)–Co(1)–O(1)	85.79(16)
N(3)–Co(1)–Cl(1)	89.76(11)	O(1)–Co(1)–Cl(1)	91.01(12)
O(1)–Co(1)–O(1A)	180.0(3)	Cl(1)–Co(1)–Cl(1A)	180.00(7)
2			
Co(1)–N(3)	2.152(3)	Co(1)–N(6B)	2.141(3)
Co(1)–O(1)	2.084(3)		
N(3)–Co(1)–N(6B)	90.89(11)	N(3)–Co(1)–O(1)	87.42(12)
O(1)–Co(1)–N(6B)	89.05(12)	N(3)–Co(1)–N(3A)	180.00(17)
N(6B)–Co(1)–N(6C)	180.0(2)	O(1)–Co(1)–O(1A)	180.0(2)

Symmetry transformations used to generate equivalent atoms: for **1** (A) $-x+1$, $-y$, $-z$; for **2** (A) $-x$, $-y$, $-z$; (B) $x+1/2$, $-y+1/2$, $z+1/2$; and (C) $-x-1/2$, $y-1/2$, $-z-1/2$.

bis(imidazole), bdc = 1,2-benzenedicarboxylate) exhibits an undulated (4,4) network. No significant supramolecular interactions such as H-bonds and π–π interactions are observed between (4,4) layers [10a]. [Zn(H_2MDP)(Mal) (H_2MDP = methylenebis(3,5-dimethylpyrazole), Mal = malonicate) has an undulated 2-D noninterpenetrating (4,4) grid network which shows the offset stacking of undulated (4,4) grids [10b]. [Co(1,4-BDC)(L)] (1,4-BDC = 1,4-benzenedicarboxylate, L = 1,1′-(2,2′-oxybis(ethane-2,1-diyl)) bis(1H-imidazole) has the highly undulated (4,4) networks, which stack parallel and no interpenetration occurs [10c]. Some undulated 2-D networks occur interpenetrating or polycatenating [11].

The uncoordinated triazole N(2) of ttmb can form hydrogen bonds with water. There are hydrogen bonding interactions between coordinated water (O(1)) and triazole nitrogen N(2) (O(1)$\cdots$Cl(1) (y, $-x+y$, and $-z$), 3.181(4) Å) and Cl^- anions

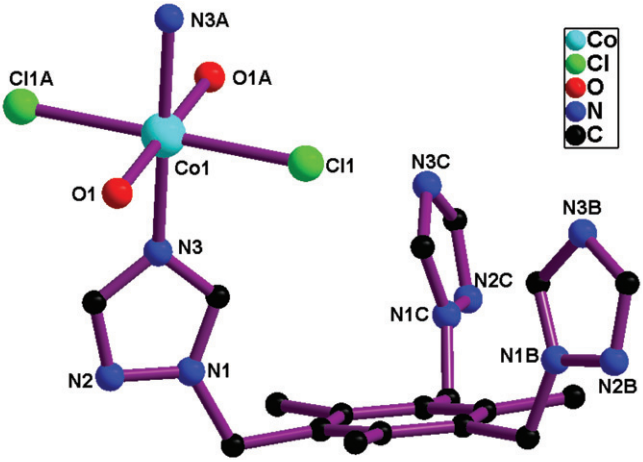


Figure 1. The coordination environment around Co(II) of **1**.

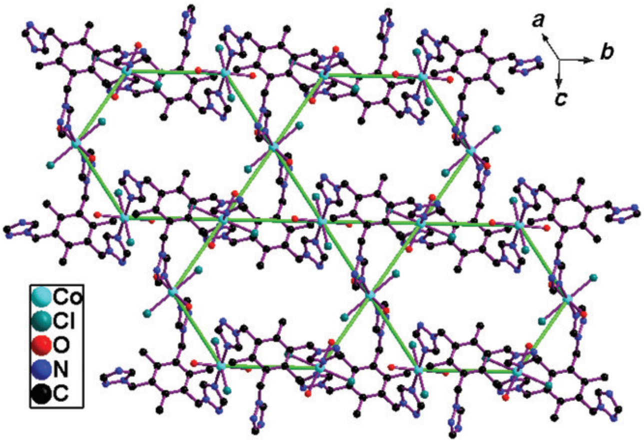


Figure 2. A 2-D network of **1**.

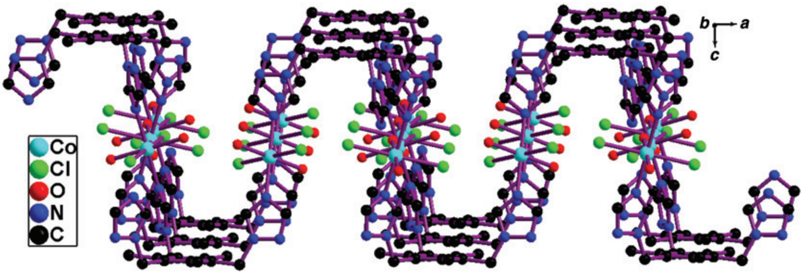


Figure 3. Side viewing an undulated 2-D network of **1** along the *b* direction.

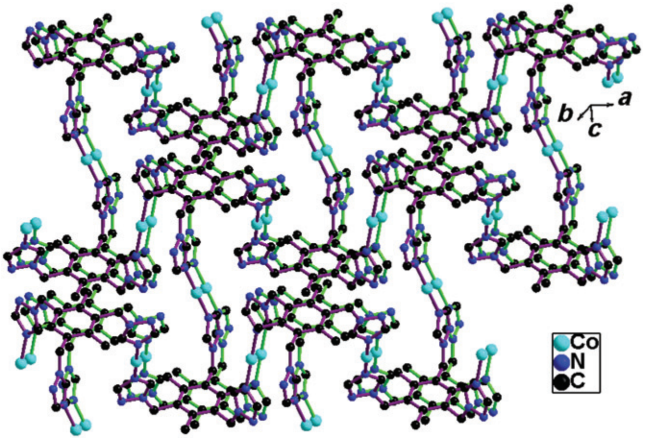


Figure 4. Two adjacent undulated 2-D networks of **1**. Note: The coordination waters and Cl^- anions are omitted for clarity.

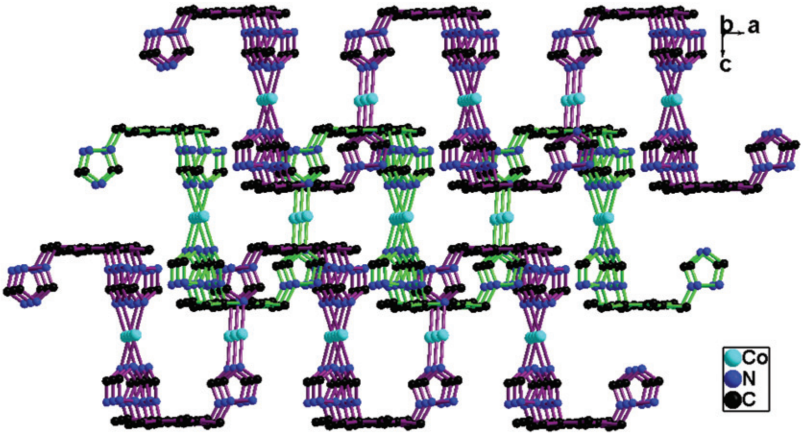


Figure 5. Three interdigitated undulated 2-D networks of **1**. Note: The coordination waters and Cl^- anions are omitted for clarity.

(O(1) $\cdots$ N(2) ($x-y-1/3$, $x-2/3$, and $-z+1/3$), 2.855(6) Å). These hydrogen bonding interactions further stabilize the 3-D network (table 3).

Structural analysis shows that **2** is a 2-D (4,4) network. The coordination geometry of cobalt(II) is distorted octahedral, coordinated by four nitrogens from four ttmb ligands (Co(1)–N(3), 2.152(3) Å; Co(1)–N(6B) 2.141(3) Å) in an equatorial plane, and two waters (Co(1)–O(1) 2.084(3) Å) in axial positions (figure 6). The Co–N and Co–O bond lengths are within normal values in **2** and similar to those in **1**.

Each ttmb shows two monodentate coordination and is double-connected. Two 4-position triazole nitrogens of ttmb coordinate cobalt(II) and one 4-position triazole nitrogen [N(9)] does not bond. The cobalt(II)s are bridged by four ttmb ligands to form a 2-D (4,4) network (figure 7). The networks contain square grids (48-membered ring) with a cobalt(II) at each corner and a ttmb ligand at each edge connecting two cobalt(II)s.

Table 3. Hydrogen bonds for **1** and **2**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (°)
1				
O(1)–H(1W)···Cl(1)^{i}	0.74(4)	2.46(4)	3.181(4)	165(5)
O(1)–H(2W)···N(2)^{ii}	0.85(5)	2.00(5)	2.855(6)	176(9)
2				
O(1)–H(1W)···O(4)^{a}	0.86(3)	1.88(3)	2.722(4)	164(5)
O(1)–H(2W)···O(6)^{b}	0.85(3)	1.80(3)	2.643(5)	173(5)

Symmetry transformations used to generate equivalent atoms: $^{i}y, -x+y, -z$; $^{ii}x-y-1/3, x-2/3, -z+1/3$ for **1**; $^{a}-x-1/2, y-1/2, -z-1/2$; $^{b}x+1, y, z$ for **2**.

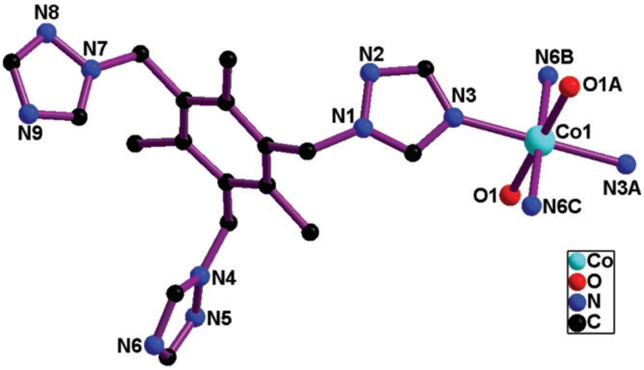


Figure 6. The coordination environment around Co(II) of **2**.

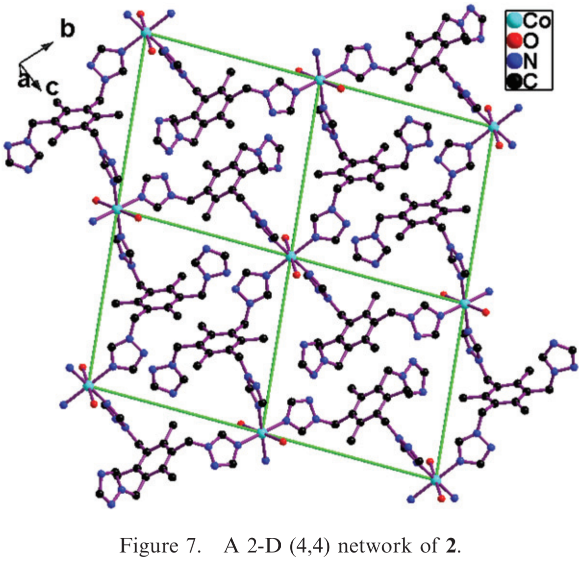


Figure 7. A 2-D (4,4) network of **2**.

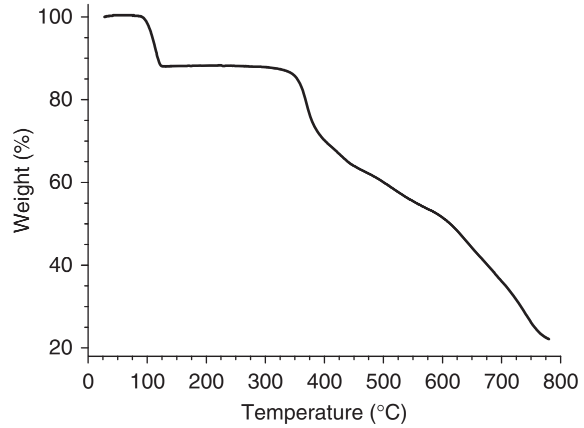


Figure 8. The TG curve of **1**.

The edge lengths are 12.127(1) Å and the inner angles are 84.838(1)° and 95.162(1)°. The ttmb shows *cis,trans,trans*-conformation in **2** compared to *cis,cis,cis*-conformation in **1**.

The 2-D networks stack parallel along *a* direction with intra-layer distance equal to the *a*-axis translation. There are hydrogen bonding interactions (table 3) between coordinated water, lattice molecules [O(1) ⋯ O(6) $(x+1, y, z)$, 2.643(5) Å], and nitrates [O(1) ⋯ O(4) $(-x-1/2, y-1/2, -z-1/2)$, 2.722(4) Å].

3.2. *Thermal stability*

Thermal analysis of **1** shows that the lattice and coordinated water are lost in a continuous fashion from 91°C to 126°C (observed: 12.15%, Calcd: 12.68%; figure 8). Anhydrous $[Co_3(ttmb)_2Cl_6]$ is stable to 323°C. Then, the complex continuously decomposes up to 781°C (observed: 55.71%) and the residue is 22.14% weight at 781°C. No reasonable fragments can be assigned corresponding to the weight loss process of **1**.

4. Conclusion

Many flexible triazole cobalt coordination polymers have been synthesized [2d, 3a, 4a–c, and 6b]. Zhao *et al.* [2d] synthesized $[Co(btp)_2(NCS)_2]$ (btp = 1,3-bis(1,2,4-triazol-1-yl)propane) with 1-D double chain structure. We synthesized eight cobalt coordination polymers with 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) [4a–c] and NO_3^-, NCS^- and dicyanamide (dca). $\{[Co(bte)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O\}_n$ (bte = 1,4-bis(1,2,4-triazol-1-yl)ethane) [4b] exhibits the undulated 2-D (4,4) network. $[Co(bte)(NCS)_2]$ contains 1-D chains bridged by double end-to-end SCN^- anions and these chains are further extended to 2-D (4,4) networks by bte bridges [4a]. $\{[Co(bte)(H_2O)_2(NCO)_2] \cdot 2H_2O\}_n$ shows the single-chain structure [4b]. $\{[Co(bte)_2(NCO)_2] \cdot H_2O\}_n$, $[Co(bte)_2(NCS)_2]_n$, and $[Co(bte)_2(dca)_2]_n$ exhibit the 1-D double-chain structures [4b, 4c]. $\{[Co(bte)(H_2O)_2(NCS)_2][Co(bte)_2(NCS)_2]\}_n$ contains both single and double chains [4b].

$\{[Co(bte)dca]_2\} \cdot H_2O\}_n$ forms a 3-D network in which each Co(II) center is bonded by two bridging bte ligands and four μ-1,5-dca in different orientations [4c]. Assemblies of 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz) and $Co(NCS)_2$ afford three supramolecular isomers $[Co(bbtz)_2(NCS)_2]_n$ of square grid networks depending on the assembly conditions. Polymer transmutation phenomena are observed among them [6b].

The self-assembly reactions of ttmb and $CoCl_2$ or $Co(NO_3)_2$ yield two 2-D network cobalt(II) coordination polymers $[Co_3(ttmb)_2(H_2O)_6Cl_6] \cdot 3H_2O$ (**1**) and $Co(ttmb)_2(H_2O)_2](NO_3)_2 \cdot 4H_2O$ (**2**). Compound **1** contains a highly undulated 2-D network. However, **2** has a 2-D (4,4) planar network. The structures of the compounds are controlled by the anions (Cl^- in **1** and NO_3^- in **2**). On the basis of this research, further syntheses and structural studies of coordination polymers with flexible tri(triazole) ligands are also under way in our laboratory.

Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, with CCDC reference numbers CCDC-760074 and 760075.

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