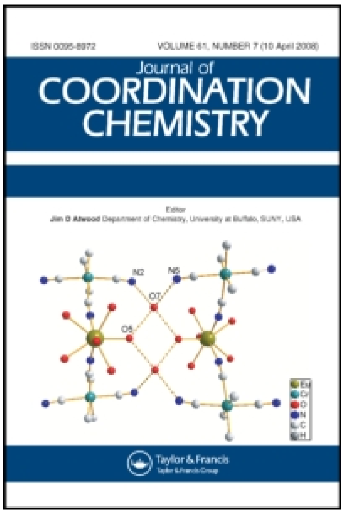

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Two novel zinc coordination polymers based on bis(1,2,4-triazole-1-yl)ethane and benzenedicarboxyl

Baolong Li[a]; Baozong Li[a]; Xia Zhu[a]; Xinhua Lu[a]; Yong Zhang[a]
[a] College of Chemistry and Chemical Engineering, The Key Laboratory of Organic Synthesis of Jiangsu Province, Suzhou University, Suzhou 215006, P. R. China

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TWO NOVEL ZINC COORDINATION POLYMERS BASED ON BIS(1,2,4-TRIAZOLE-1-YL)ETHANE AND BENZENEDICARBOXYL

BAOLONG LI*, BAOZONG LI, XIA ZHU, XINHUA LU and YONG ZHANG

College of Chemistry and Chemical Engineering,
The Key Laboratory of Organic Synthesis of Jiangsu Province,
Suzhou University, Suzhou 215006, P. R. China

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Two novel zinc complexes $[Zn_2(bte)_2(phth)_2](H_2O)_4$ (**1**) and $[Zn(bte)(terph)](H_2O)_2$ (**2**) (phth = 1,2-benzenedicarboxyl, terph = 1,4-benzenedicarboxyl, bte = bis(1,2,4-triazole-1-yl)ethane) were synthesized and characterized and their crystal structures were determined by X-ray diffraction analysis. Complex **1** crystallizes in the orthorhombic space group $Pna2_1$, with $a = 11.0742(10)$, $b = 14.4132(13)$, $c = 22.4188(18)$ Å, $V = 3578.4(5)$ Å^3, $Z = 4$; $R_1 = 0.0495$, $wR_2 = 0.1026$. Complex **2** crystallizes in the triclinic space group $\bar{P}_1$, with $a = 9.468(6)$, $b = 9.682(5)$, $c = 10.410(6)$ Å, $\alpha = 101.533(8)$, $\beta = 104.783(9)$, $\gamma = 92.042(5)°$, $V = 900.3(9)$ Å^3, $Z = 2$; $R_1 = 0.0520$, $wR_2 = 0.1193$. A two-dimensional (2D) network in **1** is formed through helical chains linking $Zn_2(phth)_2$ 14-membered rings forming 50-membered macrometallacyclic rings. The 2D rhombic network in **2** is formed through bridging terph ligands linking $Zn_2(bte)_2$ 18-membered rings.

Keywords: Crystal structure; Zinc complex; Benzenedicarboxyl; Triazole ligand; Coordination polymers

INTRODUCTION

There has been intense research in recent years on the synthesis and characterization of coordination networks with novel topologies [1–5]. Organic polycarboxyl is one of a family of excellent bridging ligands that can form coordination polymers. A large number of supramolecular structures based on multidentate polycarboxyl bridging ligands such as 1,2-benzenedicarboxyl [6], 1,4-benzenedicarboxyl [7–10], 1,3,5-benzenetricarboxylate [11], 1,2,4,5-benzenetetracarboxylate [12] and nitrilotriacetate [13] have been reported. Mixed ligand systems containing both dicarboxylates and linear bipyridine ligands have been selected for the preparation of novel coordination polymers [6,14–17]. The chemical structure of organic ligands can have a dramatic effect on network morphology. Mixed ligand systems containing both dicarboxylates and flexible bridging ligands may produce unpredictable and novel coordination polymers.

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*Corresponding author. E-mail: blli1965@pub.sz.jsinfo.net

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The flexible ligand bis(1,2,4-triazole-1-yl)ethane [18] is an effective bridging ligand [19–21]. In the present work a new mixed ligand system containing the flexible ligand bis(1,2,4-triazole-1-yl)ethane (bte) and 1,2-benzenedicarboxyl (phth) or 1,4-benzenedicarboxyl (terph) is used to construct coordination polymers. Here we report the syntheses and X-ray crystal structure analyses of two novel coordination polymers $[Zn_2(bte)_2(phth)_2](H_2O)_4$ (**1**) and $[Zn(bte)(terph)](H_2O)_2$ (**2**).

EXPERIMENTAL

All reagents were of AR grade and were used without further purification. Bis(1,2,4-triazole-1-yl)ethane (bte) was prepared following the literature method [22]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The Zn content was determined by a Leeman inductively coupled plasma (ICP) spectrometer. IR spectra were obtained as KBr pellets on a Nicolet 170SX FT–IR spectrophotometer in the 400–4000 cm^{-1} region. Thermogravimetric data were collected on a Thermal Analyst 2100 TA instrument and on an SDT 2960 TGA-DTA instrument in flowing dinitrogen at a heating rate of 10°C/min.

Synthesis of $[Zn_2(bte)_2(phth)_2](H_2O)_4$ (1) and $[Zn(bte)(terph)](H_2O)_2$ (2)

A methanol solution (15 mL) of bte (0.082 g, 0.5 mmol) was added to an aqueous solution (20 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.150 g, 0.5 mmol) and Na_2phth (0.105 g, 0.5 mmol) or Na_2terph (0.105 g, 0.5 mmol) with stirring. The resulting solutions were filtered and the filtrates were stored at room temperature. Single crystals of **1** and **2** suitable for X-ray diffraction were obtained after about 2 and 5 weeks, respectively. Elemental analysis confirmed the organic content. Anal. Calcd. for **1** $C_{28}H_{32}N_{12}O_{12}Zn_2$(%): C, 39.13; H, 3.75; N, 19.56; Zn, 15.22. Found: C, 38.97; H, 3.62; N, 19.43; Zn, 15.02. Anal. Calcd. for **2** $C_{14}H_{16}N_6O_6Zn$(%): C, 39.13; H, 3.75; N, 19.56; Zn, 15.22. Found: C, 39.04; H, 3.68; N, 19.51; Zn, 15.11. Main IR absorption bands (KBr, cm^{-1}) for **1**: 3464m, 3125w, 1659w, 1601s, 1566m, 1536m, 1485w, 1397s, 1381s, 1277w, 1208w, 1130s, 1003w, 864w, 837w, 714w, 663w and 455w. Main IR absorption bands (KBr, cm^{-1}) for **2**: 3445m, 3133w, 1589s, 1531m, 1505w, 1385s, 1377m, 1289w, 1134m, 1015w, 895w, 830w, 752m, 671w, 571w and 509w.

X-ray Structure Determination

Single crystals with dimensions $0.45 \times 0.40 \times 0.40$ mm for Complex **1** and $0.50 \times 0.28 \times 0.20$ mm for Complex **2** were selected for data collection at 193.15 K, using a RIGAKU Mercury CCD with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected by the ω-scan technique. The structures were solved by direct methods and refined using a full-matrix least-squares method (SHELX-97) [23]. The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. The parameters of the crystal, data collection and refinement are given in Table I. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (e-mail: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC numbers for **1** and **2** are 215194 and 215195, respectively.

TABLE I Crystal data and structure refinement details for compounds **1** and **2**

	[Zn$_2$(bte)$_2$(phth)$_2$](H$_2$O)$_4$ **(1)**	*[Zn(bte)(terph)](H$_2$O)$_2$* **(2)**
Empirical formula	$C_{28}H_{32}N_{12}O_{12}Zn_2$	$C_{14}H_{16}N_6O_6Zn$
Temperature (K)	193.15	193.15
Formula weight (g mol^{-1})	859.40	429.70
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	$Pna2_1$	$\bar{P}_1$
a (Å)	11.0742(10)	9.468(6)
b (Å)	14.4132(13)	9.682(5)
c (Å)	22.4188(18)	10.410(6)
α (°)	90.00	101.533(8)
β (°)	90.00	104.783(9)
γ (°)	90.00	92.042(5)
Volume (Å^3)	3578.4(5)	900.3(9)
Z	4	2
D (Mg/M^3)	1.595	1.585
Absorption coefficient (mm^{-1})	1.418	1.409
$F(000)$	1760	440
Crystal size (mm)	0.45 × 0.40 × 0.40	0.50 × 0.28 × 0.20
θ range for data collection (°)	3.07–27.48	3.23–27.48
Index ranges	$-14 \le h \le 24, -18 \le k \le 18, -28 \le l \le 28$	$-12 \le h \le 12, -12 \le k \le 10, -11 \le l \le 12$
Reflections collected	34 473	7166
Independent reflections	8088 [R(int) = 0.0482]	3925 [R(int) = 0.0222]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8088/0/487	3925/0/244
Goodness-of-fit on F^2	1.143	1.063
Final R_1 and wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0464$, $wR_2 = 0.1011$	$R_1 = 0.0463$, $wR_2 = 0.1160$
R_1 and wR_2 indices (all data)	$R_1 = 0.0495$, $wR_2 = 0.1026$	$R_1 = 0.0520$, $wR_2 = 0.1193$

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction analysis revealed that compounds **1** and **2** have completely different two-dimensional (2D) network structures.

Selected bond lengths and angles for complexes **1** and **2** are listed in Table II. In **1**, each zinc(II) atom is four-coordinate with two oxygen atoms from the COO groups of two different phth ligands and two nitrogen atoms from two bte ligands in a distorted tetrahedron (Fig. 1). Each phth coordinates two zinc(II) atoms in bis-monodentate mode [14] and each zinc is coordinated by two phth forming a $Zn_2(phth)_2$ 14-membered ring with a Zn(1)–Zn(2) distance of 5.326 Å. The bte ligands have a *gauche* conformation in **1**. The dihedral angles between N(3) and N(6), N(9) and N(12) triazole ring planes are 58.1 and 51.1°, respectively. The torsion angles N(1)–C(21)–C(22)–N(4) and N(7)–C(28)–C(27)–N(10) are 57.0(5) and 57.1(5)°, respectively. The presence of a flexible ethyl group causes the bte ligands to link zinc(II) atoms to form one-dimensional helical chains (Fig. 2). The Zn(1)–Zn(1A) separation 7.404 Å and Zn(2)–Zn(2A) 7.447 Å across the bridging bte are close to the Zn···Zn distance 8.369 Å in $[Zn(dca)_2(bte)_2]$ exhibiting Zn(*gauche*-bte)Zn [20]. The Zn···Zn distances (*ca* 7.4 Å) in **1** are shorter than the Cu···Cu distance [12.473(2) Å] in $[Cu(TTA)_2]_2(bte)$ exhibiting Cu(*anti*-bte)Cu [21]. The helical repeat distances are equal to the Zn(1)–Zn(1D) and Zn(2)–Zn(2D) separations of 11.074 and 11.074 Å, respectively. The helical chains link $Zn_2(phth)_2$ 14-membered rings forming larger

TABLE II Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

[$Zn_2(bte)_2(phth)_2](H_2O)_4$ (**1**)			
Zn(1)–O(1)	1.935(3)	Zn(1)–O(7)	1.980(3)
Zn(1)–N(3)	2.019(3)	Zn(1)–N(6A)	2.025(3)
Zn(2)–O(3)	1.985(3)	Zn(2)–O(5)	1.921(3)
Zn(2)–N(9)	2.011(3)	Zn(2)–N(12A)	2.002(4)
O(1)–Zn(1)–O(7)	106.70(13)	O(1)–Zn(1)–N(3)	112.78(13)
O(7)–Zn(1)–N(3)	96.53(13)	O(1)–Zn(1)–N(6A)	123.37(14)
O(7)–Zn(1)–N(6A)	111.61(14)	N(3)–Zn(1)–N(6A)	102.63(14)
O(3)–Zn(2)–O(5)	104.85(12)	O(3)–Zn(2)–N(9)	96.20(12)
O(5)–Zn(2)–N(9)	113.65(13)	O(3)–Zn(2)–N(12A)	111.49(13)
O(5)–Zn(2)–N(12A)	123.58(14)	N(9)–Zn(2)–N(12A)	103.80(15)
[Zn(bte)(terph)](H_2O)$_2$ (**2**)			
Zn(1)–O(1)	1.981(2)	Zn(1)–O(3)	1.966(2)
Zn(1)–N(3)	2.011(3)	Zn(1)–N(6A)	2.033(3)
O(1)–Zn(1)–O(3)	107.90(10)	O(1)–Zn(1)–N(3)	118.94(11)
O(3)–Zn(1)–N(3)	109.88(11)	O(1)–Zn(1)–N(6A)	111.07(10)
O(3)–Zn(1)–N(6A)	94.39(11)	N(3)–Zn(1)–N(6A)	111.81(11)

Symmetry code, A: $x-1/2$, $-y+1/2$, z for **1**; $-x+1$, $-y$, $-z+1$ for **2**.

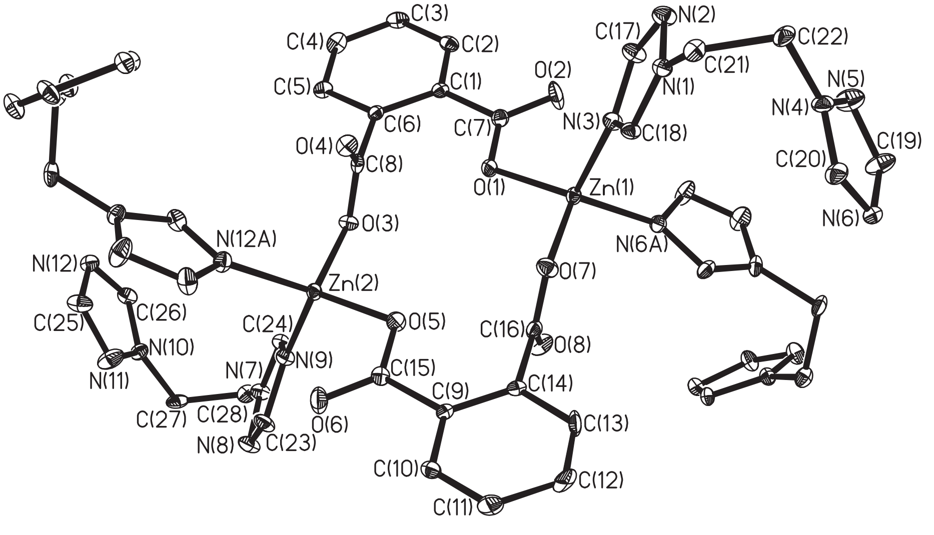

FIGURE 1 The local coordination of the Zn(II) atoms in **1**.

50-membered macrometallacyclic rings that contain four bte ligands, four phth ligands and six Zn(II) atoms in a 2D network. This 2D network is unusual. In the similar complexes $[M(4,4'\text{-bipy})(phth)(H_2O)]_n$ ($M = Co^{2+}$, Cd^{2+}), rectangular grids bridged via 4,4′-bipy and the phth dianion create a cavity-containing neutral framework [14]. A 3D network is formed in $[Co(phth)_2(4,4'\text{-bipy})]$ [6]. Water molecules fill the cavities. Hydrogen bonds are formed between solvent water molecules and the carboxylate oxygen atoms of the phth ligands [O(9)$\cdots$O(8), 2.876 Å; O(9)$\cdots$O(3), 2.916 Å; O(10)$\cdots$O(4), 2.844 Å; O(10)$\cdots$O(7), 2.943 Å; O(11) $\cdots$O(8), 2.819 Å; O(12)$\cdots$O(4), 2.854 Å]. Hydrogen bonds are also formed within solvent water molecules [O(9)$\cdots$O(11) $(x-1/2, -y+1/2, z)$, 2.962 Å; O(10)$\cdots$O(12) $(x+1/2, -y+3/2, z)$, 2.980 Å].

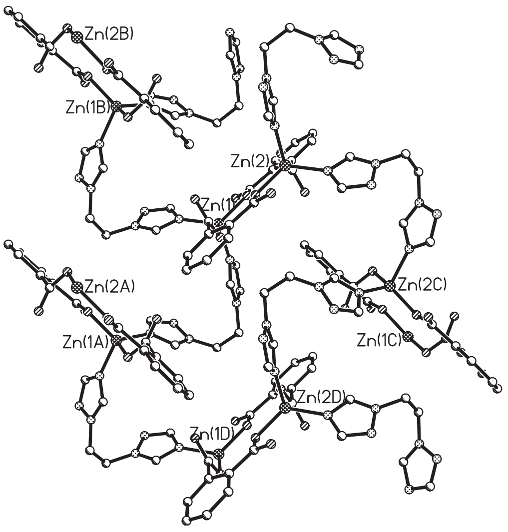

FIGURE 2 View of the 2D network containing infinite helical chains along the *c* direction in **1**.

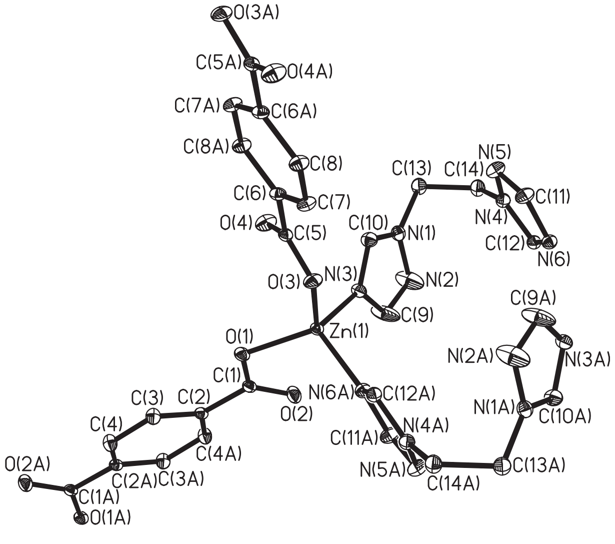

FIGURE 3 The local coordination of the Zn(II) atom in **2**.

In **2**, each zinc(II) atom is also four-coordinate with two oxygen atoms from the COO groups of two different terph ligands in bis-monodentate mode [10] and two nitrogen atoms from two bte ligands in a distorted tetrahedron (Fig. 3). In the similar compounds [M(terph)(4,4′-bipy)] ($M = Zn^{2+}$, Co^{2+}, Cd^{2+}), the zinc, cobalt and cadmium complexes have distorted trigonal bipyramidal, distorted octahedral and pentagonal bipyramidal geometry, respectively [15]. The bte ligands have a *gauche* conformation in **2**. The dihedral angle between N(3) and N(6) triazole ring planes is 57.1°. The torsion angle N(1)–C(13)–C(14)–N(4) is 51.3(4)°. Each bridging bte links two zinc(II) atoms to form $Zn_2(bte)_2$ 18-membered rings (Fig. 4) with a Zn(1)–Zn(1A) distance 6.804 Å.

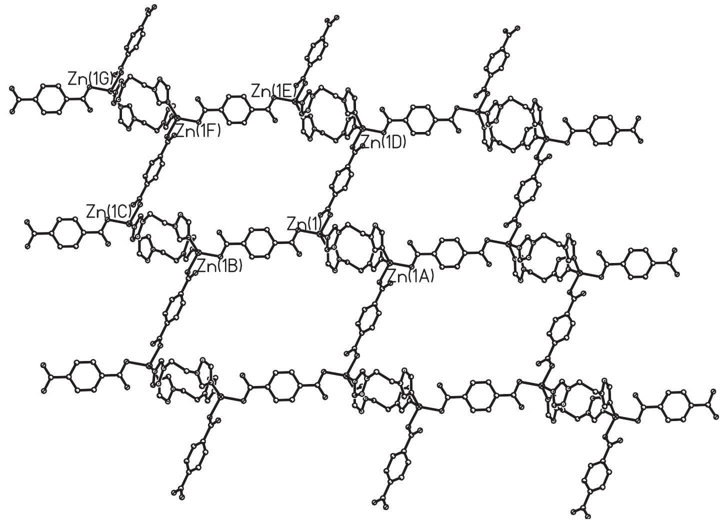

FIGURE 4 View of the 2D network containing 14-membered rings along the *c* direction in **2**.

The 6.804 Å Zn–Zn distances bridged by bte in **2** are shorter than the Zn–Zn distance of 7.404 or 7.447 Å in **1**. The bridging ligands terph link $Zn_2(bte)_2$ 18-membered rings and form a 2D rhombic network. The Zn(1)–Zn(1B) distance bridged by O(1) and O(1A) atoms is 10.926 Å and Zn(1)–Zn(1D) distance bridged by O(2) and O(2A) is 11.056 Å. The unusual 2D rhombic network is *ca* 17.0 × 11.0 Å. Similar compounds [M(terph)(4,4′-bipy)] ($M = Zn^{2+}$, Co^{2+}, Cd^{2+}) have 3D coordination networks with cuboid-like $[M_{16}(terph)_8(4,4'\text{-bipy})_8]$ as building blocks [15]. Water molecules fill the cavities. Hydrogen bonds are formed between solvent water molecules and the carboxylate oxygen atoms of the terph ligands and the uncoordinated 2-position atom of the bte ligands [O(5)···O(2) $(x+1, y, z)$, 2.798 Å; O(5)···O(4), 2.907 Å; O(6)···N(5), 3.012 Å]. Hydrogen bonds are also formed within the solvent water molecules [O(5)···O(6), 2.801 Å].

Thermogravimetric analyses were performed to investigate the thermal stability of the title compounds. Compound **1** is stable up to 184°C, although the first weight loss of 7.9% (calcd. 8.4%), which corresponds to loss of four lattice waters, occurred over the temperature range 50–127°C. Compound **2** first lost two water molecules at 40–85°C (obsd. 9.1%; calcd. 8.4%) and then gradually decomposed when the temperature reached 192°C.

In summary, two novel zinc complexes $[Zn_2(bte)_2(phth)_2](H_2O)_4$ (**1**) and $[Zn(bte)(terph)](H_2O)_2$ (**2**) with completely different 2D network structures were synthesized. The network in **1** is formed through helical chains linking $Zn_2(phth)_2$ 14-membered rings into 50-membered macrometallacyclic rings. The 2D rhombic network in **2** is formed through bridging terph ligands linking $Zn_2(bte)_2$ 18-membered rings.

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