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Blue fluorescence of three metal-organic zinc polymers containing tetrazinc units and asymmetric ligand of btc^{3-}

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Abstract

Three new zinc coordination polymers $[Zn_2(btc)_2(H_2O)_2]_n \cdot n[Zn(H_2O)_6]$ (**1**), $[Zn_3(btc)_2(2,2'\text{-bipy})_2(H_2O)_3]_n \cdot 2nH_2O$ (**2**) and $[Zn_3(btc)_2(H_2O)_6]_n \cdot nH_2O$ (**3**) (H_3btc = 1,2,4-benzenetricarboxylic acid, 2,2′-bipy = 2,2′-bipyridine) were obtained by the diffusion method and their crystal structures were determined by single-crystal X-ray diffraction. Compounds **1–3** have the similar tetrametallic unit $[Zn_4(btc)_2]$ SBUs and these SBUs are further connected into stair-like structure, 2-D layer and 3-D framework for **1**, **2** and **3**, in which the btc^{3-} ligands adopt μ_3, μ_4 and μ_5 coordination modes, respectively. The title compounds show strong blue fluorescence, which may be assigned as $\pi^* \rightarrow n$ transition of the ligand mixed with the ligand-to-metal change transfer (LMCT), indicating the fluorescence, indicates the title compounds may be good candidates for blue-light photoactive materials.

Keyword: Crystal structure; Fluorescence; SBU; Tetrazinc units; Zinc coordination polymers

1. Introduction

The domain of polycarboxylate metal-organic polymers has currently undergone extensive investigations due to their intriguing structural features, physical and chemical properties [1]. Meantime, the rigid benzene polycarboxylate acids, such as 1,4-benzenedicarboxylic acid [2,3], 1,3,5-benzenetricarboxylic acid [4,5], 1,2,4-benzenetricarboxylic acid (H_3btc) [6] and 1,2,4,5-benzenetetracarboxylic acid [7,8], with the multiplicity of the dihedral angle between the plane of the carboxylate group and the phenyl ring plane [9], have been used to bind metal centers in different directions, generating many compounds with interesting magnetic and spectroscopic properties as well as creating a great deal of multi-dimensional networks containing channels and cavities with various sizes and shapes [10]. Among these rigid ligands, 1,2,4-benzenetricarboxylic acid (H_3btc), an asymmetrical benzene polycarboxylate acid, has higher asymmetry and bigger hindrance, that can be of great benefit to the syntheses of the chiral, spiral or higher asymmetric molecules with higher dimensional structures [6].

Taking account of this, we focus our attention on the preparations and optical properties of coordination polymers with H_3btc ligand. Herein we report the syntheses and characterizations of three new high-dimensional zinc coordination polymers of $[Zn_2(btc)_2(H_2O)_2]_n \cdot n[Zn(H_2O)_6]$ (**1**), $[Zn_3(btc)_2(2,2'\text{-bipy})_2(H_2O)_3]_n \cdot 2nH_2O$ (**2**) and $[Zn_3(btc)_2(H_2O)_6]_n \cdot nH_2O$ (**3**), which are constructed from the similar parallelogramical $[Zn_4(btc)_2]$ SBUs with the btc^{3-} ligand adopting different coordination modes and show intensive blue fluorescence.

2. Experimental

2.1. General

All chemicals were commercially purchased and used without further purification. The IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellets in the range 4000–400 cm^{-1}. The electronic emission

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and excitation spectra recorded at room temperature were obtained on a computer-controlled JY FluoroMax-3 spectrometer.

2.2. Synthesis

$[Zn_2(btc)_2(H_2O)_2]_n \cdot n[Zn(H_2O)_6]$ (**1**) Aqueous solution containing H_3btc (105 mg, 0.5 mmol) and NaOH (60 mg, 1.5 mmol) were stirred for 6 h, and the 10 mL filtrate was covered with 10 mL ethanol solution of $Zn(OAc)_2 \cdot 2H_2O$ (110 mg, 0.5 mmol). Over a period of approximated 10 d, the colorless crystals of **1** were obtained. IR (cm^{-1}, KBr): 3425(vs), 2971(s), 1616(s), 1587(s), 1493(w), 1392(s), 1358(s), 1081(w), 792(w), 675(w).

$[Zn_3(btc)_2(2,2'\text{-bipy})_2(H_2O)_3]n \cdot 2nH_2O$ (**2**). Aqueous solution containing $Zn(OAc)_2 \cdot 2H_2O$ (219 mg, 1.0 mmol), H_3btc (105 mg, 0.5 mmol), and NaOH (60 mg, 1.5 mmol) were stirred for 6 h, and the 10 mL filtrate was covered with 10 mL ethanol solution of 2,2′-bipy (78 mg, 0.5 mmol). Over a period of approximated 10 d, the colorless crystals of **2** were obtained. IR (cm^{-1}, KBr): 3418(vs), 2975(s), 1660(s), 1619(s), 1401(s), 1384(s), 1131(w), 1049(w), 878(w), 619(w).

$[Zn_3(btc)_2(H_2O)_6]_n \cdot nH_2O$ (**3**). A Aqueous solution containing H_3btc (105 mg, 0.5 mmol) and NaOH (60 mg, 1.5 mmol) were stirred for 6 h, and the 10 mL filtrate was covered with 10 mL ethanol solution of $Zn(OAc)_2 \cdot 2H_2O$ (329 mg, 1.5 mmol). Over a period of approximated 10 d, the colorless crystals of **3** were obtained. IR (cm^{-1}, KBr): 3430(vs), 2974(s), 2927(s), 2345(w), 1619.19(s), 1452(s), 1394(s), 1384(s), 1088(s), 1050(w), 881(w), 609(w).

2.3. Structure determination and refinement of 1–3

Single crystals of compounds **1–3** were selected with dimensions $0.25 \times 0.30 \times 0.20$, $0.20 \times 0.15 \times 0.10$ and $0.21 \times 0.07 \times 0.10\,\text{mm}^3$, respectively. Data sets were collected on a Rigaku Mercury CCD diffractometer with ω scan technique for **1** and **2** and Rigaku AFC7R diffractometer with ω–2θ scan technique for **3**, equipped with a graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å, rotating-anode, powered at 50 kV, 150 mA). Unit cell parameters of **3** were determined by least-squares refinement using 20 reflections. The structures were solved by the direct methods and successive Fourier difference syntheses, and refined by the full matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXTL$^{\text{TM}}$) [11]. The hydrogen atoms in **1**, **2** and **3** except for water molecules were allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. Relevant crystal and data parameters are presented in Table 1.

3. Results and discussion

The colorless crystals of **1–3** suitable for X-ray diffraction were obtained from the diffusion by using zinc acetate and H3btc ligand. The present compounds are stable in air and insoluble in common polar and non-polar solvents.

Single-crystal X-ray analysis reveals that compound **1** features a 2-D stair-like structure with quadrangle channels in which the btc^{3-} ligand exhibits a μ_3 coordination mode (Scheme S1a). As shown in Fig. 1a, the Zn(1) atom is coordinated by three water molecules and their

Table 1
Crystallographic data for complexes **1–3**

	1	**2**	**3**
Color and shape	Colorless prism	Colorless prism	Colorless plate
Empirical formula	$C_{18}H_{22}O_{20}Zn_3$	$C_{38}H_{32}N_4O_{17}Zn_3$	$C_{18}H_{20}O_{19}Zn_3$
Formula weight	754.47	1012.79	736.45
T/K	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2(1)/n$	P-1	P-1
a/Å	7.435(4)	8.660(2)	7.690(2)
b/Å	9.193(4)	10.240(1)	8.884(3)
c/Å	17.375(8)	13.171(2)	10.322(2)
α/°		95.658(4)	105.69(2)
β/°	94.60(6)	100.01(4)	92.93(2)
γ/°		109.95(5)	105.59(2)
U/Å^3	1183.6(10)	1065.3(3)	648.0(3)
Z	2	1	1
D_{calcd}/g cm^{-3}	2.117	1.579	1.887
μ/cm^{-1}	31.18	17.52	28.42
Total reflections	7179	6673	2468
Unique reflections	2066	3625	2259
R_{int}	0.0207	0.0153	0.0328
Obs. reflections	1869	2541	1903
R (obs.)	$R_1 = 0.0295$, w$R_2 = 0.0910$	$R_1 = 0.0461$, w$R_2 = 0.0942$	$R_1 = 0.0529$, w$R_2 = 0.1617$
R (all)	$R_1 = 0.0328$, w$R_2 = 0.0941$	$R_1 = 0.0609$, w$R_2 = 0.0998$	$R_1 = 0.0642$, w$R_2 = 0.1759$

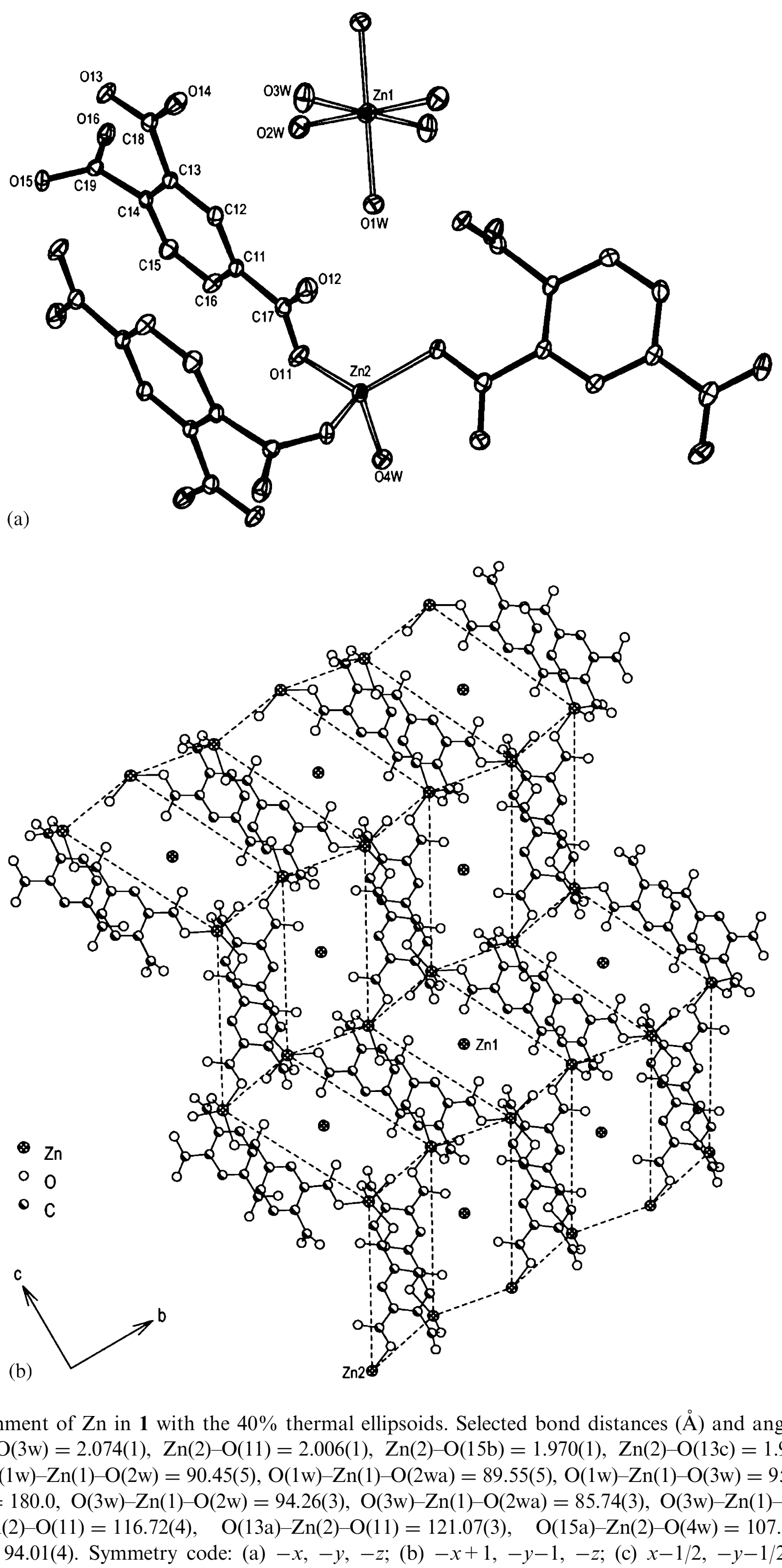


Fig. 1. (a) Coordination environment of Zn in **1** with the 40% thermal ellipsoids. Selected bond distances (Å) and angles (°): Zn(1)–O(1w) = 2.038(1), Zn(1)–O(2w) = 2.175(1), Zn(1)–O(3w) = 2.074(1), Zn(2)–O(11) = 2.006(1), Zn(2)–O(15b) = 1.970(1), Zn(2)–O(13c) = 1.976(1), Zn(2)–O(4w) = 2.018(1); O(1w)–Zn(1)–O(1wa) = 180.0, O(1w)–Zn(1)–O(2w) = 90.45(5), O(1w)–Zn(1)–O(2wa) = 89.55(5), O(1w)–Zn(1)–O(3w) = 95.78(4), O(1w)–Zn(1)–O(3wa) = 84.22(4), O(2wa)–Zn(1)–O(2w) = 180.0, O(3w)–Zn(1)–O(2w) = 94.26(3), O(3w)–Zn(1)–O(2wa) = 85.74(3), O(3w)–Zn(1)–O(3wa) = 180.0, O(15a)–Zn(2)–O(13b) = 108.79(4), O(15a)–Zn(2)–O(11) = 116.72(4), O(13a)–Zn(2)–O(11) = 121.07(3), O(15a)–Zn(2)–O(4w) = 107.13(4), O(13a)–Zn(2)–O(4w) = 106.59(4), O(11)–Zn(2)–O(4w) = 94.01(4). Symmetry code: (a) $-x$, $-y$, $-z$; (b) $-x+1$, $-y-1$, $-z$; (c) $x-1/2$, $-y-1/2$, $z-1/2$, (b) The 2-D stair-like structure with quadrangle channel of **1** with the $[Zn(1)(H_2O)_6]$ complexes locating inside the channels. The $[Zn(1)(H_2O)_6]$ cation are represented as Zn(1) atoms with the water molecules being omitted for clarity.

symmetry-related atoms to form an octahedral environment with Zn(1)–O_{water} bond distances ranging from 2.038(1) to 2.175(1) Å. The Zn(2) center is coordinated by three carboxylic oxygen atoms from three btc^{3-} ligands and one water molecule with Zn(2)–O bond lengths in the range 1.970(1)–2.018(1) Å to form a tetrahedral coordination geometry. The most important feature of **1** is that the carboxylate groups of btc^{3-} ligands adopting monodentate coordination modes bridge Zn(2) atoms into a 2-D stair-like structure. Four Zn(2) atoms are cross-bridged by two btc^{3-} ligands to form a parallelogrammical $[Zn(2)_4(btc)_2]$ SBU with the edges and the angles of the parallelogram being 4.75 and 10.22 Å, and 59.45° and 120.55°, respectively. The SBUs are inter-linked to form the step of stair with alternate array of filling and empty parallelograms along the *b*- direction and further extend to form a 2-D stair-like structure along the *c*-direction, as shown in Fig. 1b. The layers are parallel stacked to yield quadrangle channels viewing along the *a*-direction. The $[Zn(1)(H_2O)_6]$ complexes are located between the layers and fill the channels, which link the layers into 3-D framework through O⋯O hydrogen bonds (Fig. S1).

Compound **2** is the first example in which the btc^{3-} ligand exhibits μ_4 coordination mode and three carboxylate groups adopt monodentate and bidentate coordination fashions in the $\{M/btc^{3-}\}$ system (Scheme S1b) [6]. As shown in Fig. 2a, the Zn(1) center is coordinated by one oxygen atom from btc^{3-} ligand, two water molecules and their symmetry-related atoms with Zn(1)–O ranging from 2.243(3) to 2.371(1) Å to form an octahedral environment with O(2W), O(2Wa), O(11) and O(11a) ($a = 1 - x$, $1-y$, $1-z$) atoms lying on the equatorial plane and the axial positions being occupied by O(1W) and O(1Wa) atoms. While the Zn(2) center displays a distorted trigonal bipyramidal ZnO_3N_2 coordination environment with $\tau = 0.259$ ($\tau = (\beta-\alpha)/60$, α and β being the bigger bond angles around Zn centers; $\tau = 0$ for ideal square pyramid; and $\tau = 1$ for ideal trigonal bipyramid) [12]. The trigonal bipyramid geometry of the Zn(2) atom is comprised of two nitrogen atoms from one 2,2′-bipy ligand and three carboxylic oxygen atoms from three btc^{3-} ligands with O(15b), O(14c) ($b = -x$, $-y+2$, $-z+1$; $c = -x$, $-y+1$, $-z+1$) and N(22) atoms lying on the equatorial plane and the axial positions being occupied by O(12) and N(21) atoms. The average Zn(2)–N bond distances is 2.334(2) Å and the Zn(2)–O bond lengths range from 2.228(2) to 2.341(1) Å. Similar to **1**, four Zn(2) atoms are bridged by two parallel btc^{3-} ligands to form a parallelogrammical $[Zn(2)_4(btc)_2]$ SBU with size of 10.24×6.24 Å^2, which are edge-sharing to each other to form an 1-D linear ladder with the 2,2′-bipy ligands perpendicularly chelating to the Zn(2) atoms on the both sides of ladder extending along the *b*-direction, as shown in Fig. 2b. These ladders are bridged by $[Zn(1)(H_2O)_4]$ units to form a 2-D layer through the Zn(1)–O(11) bonds with the btc^{3-} ligand displaying μ_4–η^2, η^1, η^1 coordination modes along the *a*-direction (Fig. 2c). The layers are further connected together to form a 3-D framework by hydrogen bonds and π–π stacking interactions between neighboring 2,2′-bipy with the centroid–centroid distance of 3.869 Å (Fig. S2).

Unlike **1** and **2**, compound **3** features a 3-D structure with quadrangle channel in which the btc^{3-} ligand adopts a μ_5 coordination mode (Scheme S1c) and is isomorphous with the analog of cadmium carboxylate [9]. As shown in Fig. 3a, Zn(1) atom is coordinated by one oxygen atoms from btc^{3-} ligands and two water molecules and their symmetry-related atoms to form an octahedral geometry with four coordinated water molecules lying on the equatorial plane and the axial positions being occupied by two oxygen atoms from btc^{3-} ligands. Similar to Zn(1), the Zn(2) atom exhibits a pseudo-octahedral configuration and is coordinated by five carboxylic oxygen atoms from four btc^{3-} ligands with O(13b), O(15c), O(16c) ($b = -x$, $-y+1$, $-z+1$; $c = -x$, $-y+1$, $-z+2$) and O(3W) atoms lying on the equatorial plane and the axial positions being occupied by the O(12d) and O(14) ($d = x-1$, y, z) atoms. The Zn–O distances vary from 2.266(2) to 2.334(3) Å for Zn(1) atom and from 2.224(2) to 2.421(2) Å for Zn(2) atom. The most attention-getting feature of **3** is that the carboxylate groups of btc^{3-} ligand adopting bidentate and chelating coordination modes bridge Zn(2) atoms into a 2-D stair-like layer along the *ac* plane with the carboxylic O(11) atoms spreading out the both sides of layer (Fig. 3b). Unlike **1**, in which the stair-like layer can be regarded as constructing from the interlinkage of filling and empty steps alone the *b*-direction, in **3** the ladder-like steps are formed by edge-sharing the parallelograms of $[Zn(2)_4(btc)_2]$ SBUs with a size of 5.66×10.32 Å^2 extending along the *c*-direction, as the case found in **2**, and further extended into stair-like layer via Zn(2)–O(14) bonds along the *a*-direction. The layers are bridged by Zn(1) complexes via Zn(1)–O(11) bonds to form a 3-D framework along the *b*-axis containing quadrangle channels with the size 14.41×5.88 Å^2 along the *a*-direction (Fig. 3c). The lattice water molecules are located inside the channels and make hydrogen bonds with O(3W) and O(15) atoms to consolidate the crystal structure of **3** (Fig. 3c). According to the reaction proportions of the starting materials, it is obvious that with increasing the molar ratio of the Zn^{2+}:H_3btc:NaOH from 1:1:3 to 3:1:3, the coordination number of btc^{3-} ligand change from μ_3 to μ_5 and the final structures vary from 2-D layer to 3-D framework, which proves the fact that increasing proportions of the metal ion can lead to the more complicated framework [13]. As shown in Scheme 1, the 2-D structure of **1** contains three non-coordinated carboxylic oxygen atoms of each btc^{3-} ligand spreading out the both sides of plane of the SBU with the dihedral angle between the phenyl ring and the parallelogram being 47.33(3)°, in which the three non-coordinated carboxylic oxygen atoms have the ability to further coordinate to metal ions along the approximately perpendicular direction of the plane of SBU. In order to obtain the coordination polymers with more high-dimensional structure, the molar ratio of metal salt to ligand has been increased in the synthetic procedures. In comparison with **1**, the molar ratio of zinc salt to H_3btc ligand was increased to 2:1 and compound **2** featured 2-D structure with the btc^{3-} ligand adopting μ_4 coordination mode with the dihedral angle between the phenyl ring and the parallelogram being 32.19(6)° was

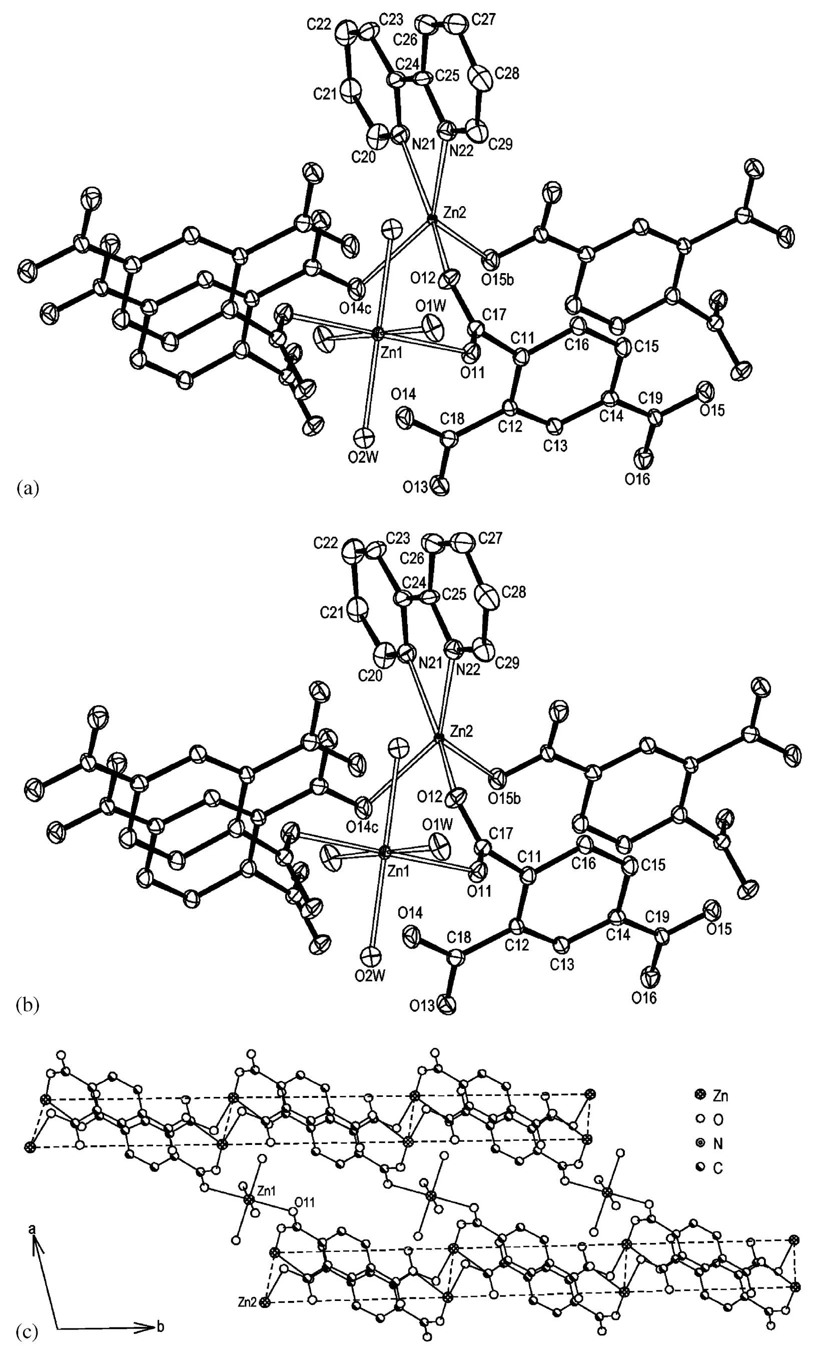


Fig. 2. (a) Coordination environment of Zn atoms in **2** with the 10% thermal ellipsoids. Selected bond distances (Å) and angles (°): Zn(1)–O(2w) = 2.243(3), Zn(1)–O(1w) = 2.2446(14), Zn(1)–O(11) = 2.3709(14), Zn(2)–O(12) = 2.2834(15), Zn(2)–O(14c) = 2.3406(13), Zn(2)–O(15b) = 2.2278(15), Zn(2)–N(22) = 2.3297(15), Zn(2)–N(21) = 2.3373(19); O(1w)–Zn(1)–O(1wa) = 180.0, O(1w)–Zn(1)–O(11) = 90.64(5), O(1W)–Zn(1)–O(11a) = 89.36(5), O(1wa)–Zn(1)–O(11a) = 90.64(5), O(2w)–Zn(1)–O(2wa) = 180.0, O(2w)–Zn(1)–O(1w) = 91.91(7), O(2w)–Zn(1)–O(1wa) = 88.09(7), O(2wa)–Zn(1)–O(1wa) = 91.91(7), O(2w)–Zn(1)–O(11) = 89.81(8), O(2W)–Zn(1)–O(11a) = 90.19(8), O(11)–Zn(1)–O(11a) = 180.0, O(12)–Zn(2)–N(22) = 88.68(6), O(12)–Zn(2)–N(21) = 156.73(6), O(12)–Zn(2)–O(14c) = 89.40(6), O(15b)–Zn(2)–O(12) = 105.05(6), O(15b)–Zn(2)–N(22) = 131.74(5), O(15b)–Zn(2)–N(21) = 97.44(6), O(15b)–Zn(2)–O(14c) = 85.93(5), N(21)–Zn(2)–O(14c) = 98.16(6), N(22)–Zn(2)–N(21) = 71.65(6), N(22)–Zn(2)–O(14c) = 141.22(6). Symmetry code: (a) $-x+1$, $-y+1$, $-z+1$; (b) $-x$, $-y+2$, $-z+1$; (c) $-x$, $-y+1$, $-z+1$, (b) 1-D ladder of **2** constructed by parallelogrammical $[Zn(2)_4(btc)_2]$ SBUs with by 2,2′-bipy ligands cheating Zn(2) atoms on the both sides of ladder, (c) 2-D layer of **2** formed by bridging ladders through $[Zn(1)(H_2O)_4]$ units.

obtained, in which each btc^{3-} ligand contains two non-coordinated carboxylic oxygen atoms lying near the plane of SBU. By increasing the molar ratio to 3:1, compound **3** featured 3-D structure was obtained, and the btc^{3-} ligand adopted μ_5 coordination mode with the dihedral angle between the phenyl and the parallelogram being 32.60(8)°, in which the six carboxylic oxygen atoms of each btc^{3-} ligand all coordinated to metal atoms. In addition, 2,2′-bipy

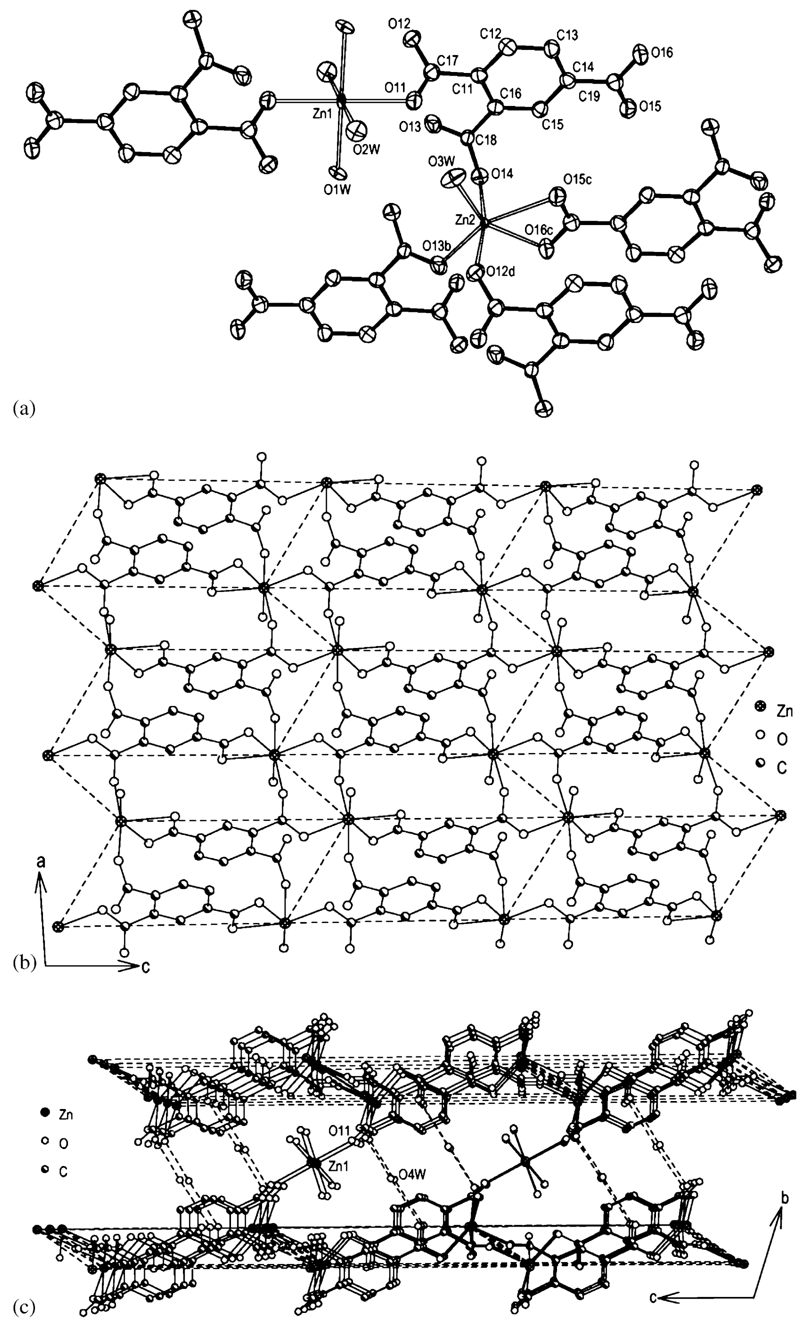
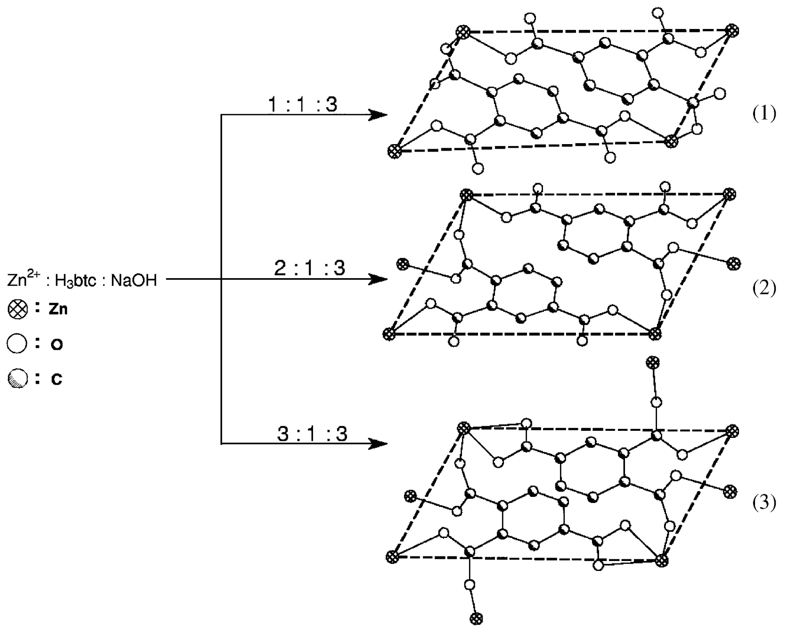


Fig. 3. (a) Coordination environment of Zn atoms in **3** with the 30% thermal ellipsoids. Selected bond distances (Å) and angles (°): Zn(1)–O(1w) = 2.334(3), Zn(1)–O(2w) = 2.280(2), Zn(1)–O(11) = 2.266(2), Zn(2)–O(3w) = 2.242(2), Zn(2)–O(12d) = 2.318(2), Zn(2)–O(13b) = 2.224(2), Zn(2)–O(14) = 2.336(2), Zn(2)–O(15c) = 2.421(2), Zn(2)–O(16c) = 2.293(2); O(1w)–Zn(1)–O(1wa) = 180.0, O(2w)–Zn(1)–O(1w) = 84.30(10), O(2w)–Zn(1)–O(1wa) = 95.70(10), O(2wa)–Zn(1)–O(1wa) = 84.30(10), O(2w)–Zn(1)–O(2wa) = 180.0, O(11)–Zn(1)–O(2w) = 89.39(9), O(11)–Zn(1)–O(2wa) = 90.61(9), O(11a)–Zn(1)–O(1w) = 90.81(10), O(11)–Zn(1)–O(1w) = 89.19(10), O(11a)–Zn(1)–O(11) = 180.0, O(3w)–Zn(2)–O(16c) = 147.95(9), O(3w)–Zn(2)–O(12d) = 80.81(8), O(3W)–Zn(2)–O(14) = 96.59(8), O(3W)–Zn(2)–O(15c) = 93.38(9), O(12d)–Zn(2)–O(15c) = 100.65(8), O(12d)–Zn(2)–O(14) = 169.25(8), O(13b)–Zn(2)–O(3w) = 114.31(10), O(13b)–Zn(2)–O(16c) = 97.60(8), O(13b)–Zn(2)–O(12d) = 83.70(8), O(13b)–Zn(2)–O(14) = 87.95(8), O(13b)–Zn(2)–O(15c) = 152.29(8), O(14)–Zn(2)–O(15c) = 89.89(8), O(16c)–Zn(2)–O(12d) = 100.63(8), O(16c)–Zn(2)–O(14) = 87.14(8), O(16c)–Zn(2)–O(15c) = 54.70(7). Symmetry code: (a) $-x+1$, $-y+2$, $-z+1$; (b) $-x$, $-y+1$, $-z+1$; (c) $-x$, $-y+1$, $-z+2$; (d) $x-1$, y, z, (b) Stair-like layer of **3** formed by the inter-linkage of filling and empty steps and the filling steps constructed by edge-sharing the $[Zn(2)_4(btc)_2]$ SBUs, (c) 3-D framework of **3** constructed by bridging layers through Zn(1) units and stabilized by hydrogen-bonding interaction (broken lines).



Scheme 1. The relations of molar ratios of the reactants and structures with different coordination mode of btc^{3-} ligand.

Table 2
Dihedral angles (°) between the planes of the 1, 2, 4-carboxylate groups and the phenyl ring of H3btc3- ligand in **1–3**

Compounds	1-carboxylate group	2-carboxylate group	4-carboxylate group
1	82.89	5.87	4.61
2	78.18	7.39	5.42
3	69.41	37.95	4.12

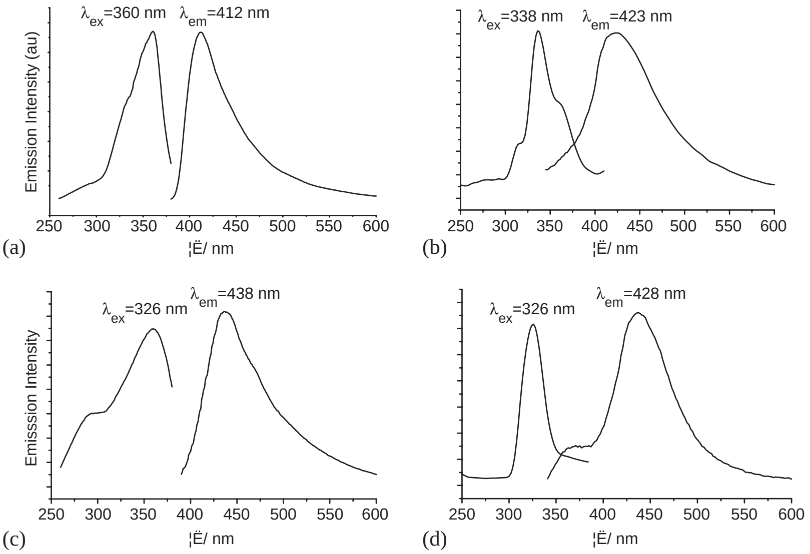


Fig. 4. The excitation and emission spectra of pure H_3btc (a), **1** (b), **2** (c), and **3** (d) recorded at room temperature.

may be the minor factor of affecting the coordination mode of btc^{3-} ligand and the structure of compound **2**. Like water molecules, 2,2′-bipy may only enhance the steric hindrance by holding one of Zn^{2+} coordination positions, but not extend the whole structure of a compound.

In the tetrazinc parallelogrammical SBUs, there exist different dihedral angles between the planes of the 1,2,4-carboxylate groups and the phenyl ring plane (Table 2). In comparison with **1** and **2**, in which only one of the two oxygen atoms of the 2-carboxylate group coordinates to Zn atom, in **3** two oxygen atoms bind to two Zn atoms resulting in the formation of a larger dihedral angle between the plane of 2-carboxylate group and the phenyl ring plane.

The excitation and emission spectra of **1–3** and pure H_3btc ligand in the solid state show the emissions of the present compounds are red-shift in comparison with that of pure ligand, as shown in Fig. 4. The emission peak of H_3btc centers at 412 nm with the excitation at 360 nm, which is attributable to the $\pi^* \rightarrow n$ transitions [14]. Interestingly, the emission spectra of **1–3** show intensive peaks around 430 nm, which are similar to the case found in zinc polycarboxylate acid compounds [15], and the enhanced fluorescence of present compounds is probably attributed to the more rigidity of the ligand coordinated to Zn^{2+} ion than that of the free ligand, which effectively reduces the loss of energy [16,17]. Therefore, the strong blue fluorescence of the present compounds may be related to the $\pi^* \rightarrow n$ transition of the ligand mixed with the ligand-to-metal change transfer (LMCT).

In the IR spectra of the compounds, the characteristic peaks of $v(H_2O)$ appeared at 3425, 3418 and 3430 cm^{-1} for **1**, **2** and **3**, respectively. Specifically, absorption for the antisymmetric stretching vibrations $v_{as}(COO^-)$ were observed at 1616 cm^{-1} for **1**, 1619 cm^{-1} for **2**, and 1619 cm^{-1} for **3**. Symmetric stretching vibrations $v_s(COO^-)$ were shown at 1392 cm^{-1} for **1**, 1401 and 1384 cm^{-1} for **2**, 1394 and 1384 cm^{-1} for **3**. The difference $\Delta(v_{as}(COO^-)$-$v_s(COO^-))$ were on the order of 200 cm^{-1} and the above stretches were shifted to lower values compared to the carbonyl frequencies of free H_3btc ligand, indicating the carboxylate groups in the compounds coordinated to the Zn ions [18].

4. Conclusion

In summary, we have successfully combined the merits of Zn metal and H_3btc ligand to synthesize three metal-organic polymers with different coordination modes and different dimensional frameworks. Comparing three compounds, it has been found that increasing proportions of the metal ion can influence the coordination modes of ligand and further lead to the more complicated framework. Furthermore, strong blue fluorescence indicates the title compounds may be good candidates for blue-light photoactive materials.

5. Supplementary material

Crystallographic data for **1**, **2** and **3** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC-254562, 254563 and 254564). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the on-line version at doi:10.1016/j.jssc.2005.08.024.

References

[1] (a) C.N.R. Rao, S. Natarajan, R. Vaidhyanathan, Angew. Chem., Int. Ed. 43 (2004) 1466;
(b) S.V. Ganesan, S. Natarajan, Inorg. Chem. 43 (2004) 198.

[2] (a) T.M. Reineke, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Angew. Chem., Int. Ed. Engl. 38 (1999) 2590;
(b) M. Edgar, R. Mitchell, A.M.Z. Slawin, P. Lightfoot, P.A. Wright, Chem.Eur. J. 7 (2001) 5168;
(c) A.D. Cutland, J.A. Halfen, J.W. Kampf, V.L. Pecoraro, J. Am. Chem. Soc. 123 (2001) 6211;
(d) K. Barthelet, J. Marrot, G. Ferey, D. Riou, Chem. Commun. (2004) 520.

[3] (a) N. Das, P.S. Mukherjee, A.M. Arif, P.J. Stang, J. Am. Chem. Soc. 125 (2003) 13950;
(b) Y.-C. Liao, F.-L. Liao, W.-K. Chang, S.-L. Wang, J. Am. Chem. Soc. 126 (2004) 1320;
(c) T. Loiseau, H. Muguerra, G. Ferey, M. Haouas, F. Taulelle, J. Solid. State. Chem. 178 (2005) 621.

[4] (a) S.S. Chui, S.M. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, Science 283 (1999) 1148;
(b) M.P. Suh, J.W. Ko, H.J. Choi, J. Am. Chem. Soc. 124 (2002) 10976;
(c) J. Zhu, X.H. Bu, P.Y. Feng, G.D. Stucky, J. Am. Chem. Soc. 122 (2000) 11563;
(d) T.J. Prior, M.J. Rosseinsky, Inorg. Chem. 42 (2003) 1564.

[5] (a) A. Dimos, A. Michaelides, S. Skoulika, Chem. Mater. 12 (2000) 3256;
(b) L. Pan, E.B. Woodlock, X.T. Wang, C. Zheng, Inorg. Chem. 39 (2000) 4174;
(c) F.A. Cotton, C. Lin, C.A. Murillo, Inorg. Chem. 40 (2001) 6413;
(d) D. Cheng, M.A. Khan, R.P. Houser, Inorg. Chem. 40 (2001) 6858.

[6] (a) M.J. Plater, M.R.St.J. Foreman, R.A. Howie, J.M.S. Skakle, A.M.Z. Stawin, Inorg. Chem. Acta. 315 (2001) 126;
(b) J. Fan, H.-F. Zhu, T. Okamura, W.-Y. Sun, W.-X. Tang, N. Ueyama, New. J. Chem. (Nouv. J. Chem). 27 (2003) 1409;
(c) M. Riou-Cavellec, C. Lesaint, M. Nogues, J.-M. Greneche, G. Ferey, Inorg. Chem. 42 (2003) 5669;
(d) L. Wang, Z. Shi, G.H. Li, Y. Fan, W.S. Fu, S.H. Feng, Solid State Sci. 6 (2004) 85;
(e) N. Hao, E.H. Shen, Y.G. Li, E.B. Wang, C.W. Hu, L. Xu, Inorg. Chem. Commun. 7 (2004) 131;
(f) C. Qin, X.L. Wang, E.B. Wang, C.W. Hu, L. Xu, Inorg. Chim. Acta. 357 (2004) 3683.

[7] (a) N. Snejko, E. Gutierrez-Puebla, J.L. Martinez, M.A. Monge, C. Ruiz-Valero, Chem. Mater. 14 (2002) 1879;
(b) M. Sanselme, J.M. Greneche, M. Riou-Cavellec, G. Ferey, Chem. Commun. (2002) 2172;
(c) R. Cao, D.F. Sun, Y.C. Liang, M.C. Hong, K. Tatsumi, Q. Shi, Inorg. Chem. 41 (2002) 2087;

(d) L.-J. Zhang, J.-Q. Xu, Z. Shi, W. Xu, T.-G. Wang, J. Chem. Soc., Dalton Trans. (2003) 1148.

[8] (a) H. Kumagai, C.J. Kepert, M. Kurmoo, Inorg. Chem. 41 (2002) 3410;
(b) D.P. Cheng, M.A. Khan, R.P. Houser, J. Chem. Soc., Dalton Trans. (2002) 4555;
(c) S. Tashiro, M. Tominaga, T. Kusukawa, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, Angew. Chem., Int. Ed. Engl. 42 (2003) 3276;
(d) S.V. Ganesan, S. Natarajan, Inorg. Chem. 43 (2004) 198.

[9] J. Fan, H.-F. Zhu, Taka-aki Okamura, W.-Y. Sun, W.-X. Tang, Norikazu Ueyama, New J. Chem. 27 (2003) 1409.

[10] (a) H.L. Li, M. Eddaoudi, M. O' Keeffe, O.M. Yaghi, Nature 402 (1999) 276;
(b) L. Pan, N.W. Zhang, Y.G. Wu, S. Han, R.Y. Yang, X.Y. Huang, J. Li, Inorg. Chem. 40 (2001) 828;
(c) J.C. Dai, X.T. Wu, Z.Y. Fu, S.M. Hu, W.X. Du, C.P. Cui, L.M. Wu, H.H. Zhang, R.Q. Sun, Chem. Commun. (2002) 12;
(d) J.W. Wo, K.S. Min, M.P. Suh, Inorg. Chem. 41 (2002) 2151;
(e) W. Chen, J.-Y. Wang, C. Chen, Q. Yue, h.-m. Yuan, J.-S. Chen, S.-N. Wang, Inorg. Chem. 42 (2003) 944.

[11] Siemens, SHELXTL^{TM} Version 5 Reference Manual, Siemens Engergy & Automation Inc., Madison, Wisconsin, 1994, USA.

[12] A.W. Addision, T.N. Rao, J. Reedjik, J. Van Riju, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349–1356.

[13] S.A. Barnett, A.J. Blake, N.R. Champness, J.E.B. Nicolson, C. Wilson, J. Chem. Soc., Dalton Trans. (2001) 567.

[14] W. Chen, J.-Y. Wang, C. Chen, Q. Yue, H.-M. Yuan, J.-S. Chen, S.-N. Wang, Inorg. Chem. 42 (2003) 944.

[15] (a) J. Tao, M.L. Tong, J.X. Shi, X.M. Chen, S.W. Ng, Chem. Commun. (2000) 2043;
(b) J. Tao, J.X. Shi, M.L. Tong, X.X. Zhang, X.M. Chen, Inorg. Chem. 40 (2001) 6328.

[16] L. Yi, L.-N. Zhu, B. Ding, P. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang, Inorg. Chem. Commun. 6 (2003) 1209.

[17] L. Xu, G.-C. Guo, B. Liu, M.-S. Wang, J.-S. Huang, Inorg. Chem. Commun. 7 (2004) 1145.

[18] (a) K. Nakamoto, Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986;
[b] G.B. Deacon, R. Philips, J. Coord. Chem. Rev. 33 (1980) 227;
(c) C. Djordjevic, M. Lee, E. Sinn, Inorg. Chem. 28 (1989) 719.