

Four transition metal complexes constructed with mixed mercaptotetrazole and 4,4'-bipyridine ligands

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Received: 21 April 2013 / Accepted: 24 June 2013 / Published online: 7 July 2013
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Abstract Based on 5-mercapto-1H-tetrazole-1-methanesulfonic acid disodium salt (Na_2mtms) and 4,4'-bipyridine (bpy) as ligands, four new transition metal complexes, namely $\{[\text{Cd}_2(\text{mtms})(\text{bpy})_2(\text{OAc})_2]\cdot\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Cd}(\text{mtms})(\text{bpy})_2(\text{H}_2\text{O})_2]_2\cdot\text{bpy}\cdot 4\text{H}_2\text{O}\}_n$ (**2**), $\{[\text{Zn}_2(\mu_2\text{-OH})(\text{mtms})(\text{bpy})_3(\text{H}_2\text{O})]\cdot\text{ClO}_4\cdot\text{H}_2\text{O}\}_n$ (**3**), and $\{[\text{Co}(\text{mtms})_2(\text{bpy})(\text{H}_2\text{O})_2]\cdot[\text{Co}(\text{bpy})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ (**4**), have been synthesized and characterized by single-crystal X-ray diffraction. Complex **1** features a pillared-layer coordination architecture linked by acetate, mtms, and bridging bpy ligands. Complex **2** has a 1D polymeric structure with $[\text{Cd}(\text{mtms})(\text{bpy})_2(\text{H}_2\text{O})_2]$ as the repeating unit; these infinite chains are further connected into a 3D supramolecular framework through π - π stacking of bpy ligands. In complex **3**, the mtms ligand combined with μ_2 -OH bridges two Zn atoms to form a dimer structure, which is different from that of complex **2**. Complex **4** shows a 3D supramolecular network containing infinite $[\text{Co}(\text{mtms})_2(\text{bpy})(\text{H}_2\text{O})_2]^{2-}$ anionic chains and free $[\text{Co}(\text{bpy})_2(\text{H}_2\text{O})_4]^{2+}$ cationic components. The luminescence

properties of **1** and **2** and the electrochemical properties of **3** are reported.

Introduction

Chemical templates have an important role in the formation of complexes containing multiple components that have defined structural assemblies [1, 2]. Several previous studies have shown that geometries and sizes of ligands, the coordinating ability of anions, and the nature of metals are all important in determining the structures of such complexes [3–8]. *N*-heterocycles with sulfhydryl ligands are capable of $-\text{N}(\text{H})-\text{C}(=\text{S}) \leftrightarrow -\text{N}=\text{C}(-\text{SH})$ tautomerization. Heterocyclic nitrogen can participate in coordination, while the sulfhydryl moiety can be used as a bridging group [8–14]. The soft sulfhydryl group has good coordination ability, because it has empty *3d* orbital that can accept electrons from the metal [8, 14–16]. Recently, research into nitrogen heterocycles with sulfhydryl ligands has mainly concentrated on sulfhydryl imidazole, sulfhydryl-(1,2,4)-triazole, and sulfhydryl tetrazole [8, 14, 17–19]. In our previous studies, we have reported some novel coordination polymers with 5-mercapto-1H-tetrazole-1-acetic acid [17]. In addition, bis- or multidentate ligands based on bipyridine (bpy) are outstanding bridging ligands, and a number of frameworks have been synthesized [20, 21]. Normally, 4,4'-bpy is an effective rodlike linker joining metal atoms for propagation of coordination networks [14, 21, 22].

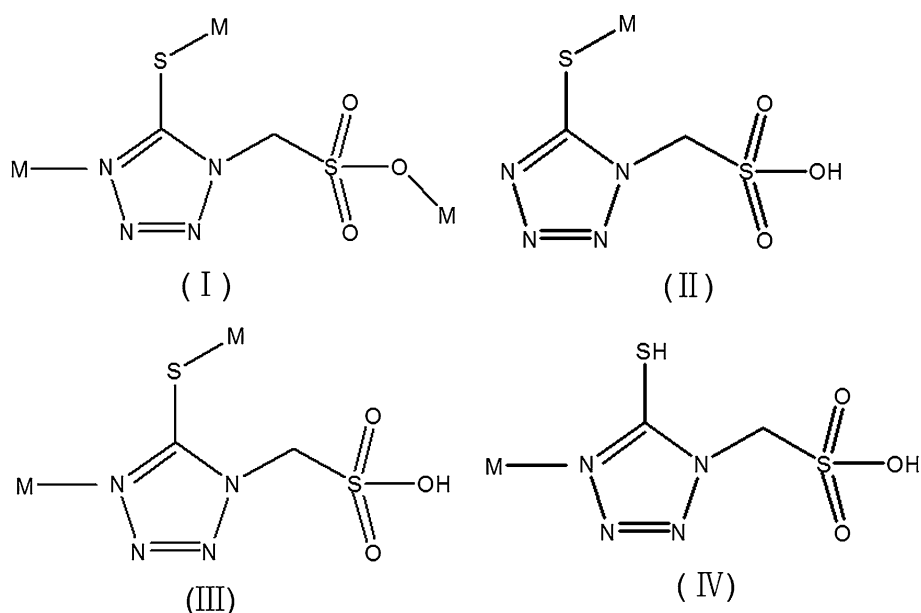
Herein, we present four transition coordination polymers containing mtms (Scheme 1) and bpy (Scheme 2) co-ligands, namely $\{[\text{Cd}_2(\text{mtms})(\text{bpy})_2(\text{OAc})_2]\cdot\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Cd}(\text{mtms})(\text{bpy})_2(\text{H}_2\text{O})_2]_2\cdot\text{bpy}\cdot 4\text{H}_2\text{O}\}_n$ (**2**), $\{[\text{Zn}_2(\mu_2\text{-OH})(\text{mtms})(\text{bpy})_3(\text{H}_2\text{O})]\cdot\text{ClO}_4\cdot\text{H}_2\text{O}\}_n$ (**3**), and $\{[\text{Co}(\text{mtms})_2(\text{bpy})(\text{H}_2\text{O})_2]\cdot[\text{Co}(\text{bpy})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}\}_n$ (**4**).

Electronic supplementary material The online version of this article (doi:[10.1007/s11243-013-9746-0](https://doi.org/10.1007/s11243-013-9746-0)) contains supplementary material, which is available to authorized users.

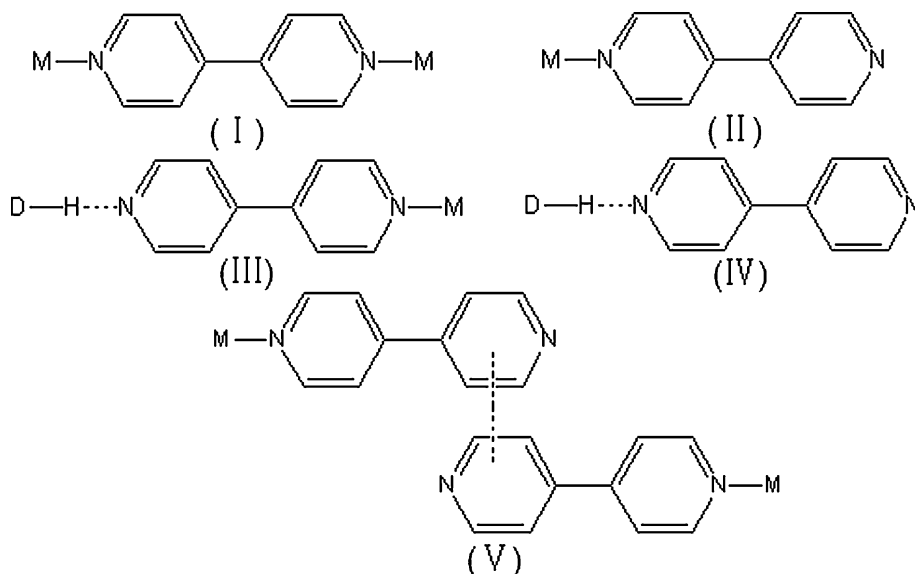
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Scheme 1 The four coordination modes of mtms ligand observed in this work



Scheme 2 The five coordination modes of bpy ligand observed in this work



Experimental

Materials and measurements

All reagents were commercially available and used without further purification. Elemental analyses for C, H, N, and S were carried out with a Perkin-Elmer 2400II elemental analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with KBr pellets in the range $4,000\text{--}400\text{ cm}^{-1}$. Electrochemical measurements were made at room temperature using a BAS Epsilon electrochemical workstation with a conventional three-electrode cell consisting of a glassy carbon working electrode, a platinum auxiliary, and a saturated calomel

reference electrode (SCE). KCl (0.1 mol L^{-1}) was used as a supporting electrolyte in aqueous solution.

Synthesis of complex 1

Bipyridine (77.8 mg, 0.5 mmol) was added to a stirred solution of Na_2mtms (120.6 mg, 0.5 mmol) and $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (274.0 mg, 1 mmol) in a mixture of 15 ml (1:1) $\text{H}_2\text{O}/\text{EtOH}$. The mixture was stirred under reflux for 3 h and then filtered. After a month, colorless block crystals were obtained from the filtrate. Yield: 60%. Anal. Calc. for $\text{C}_{26}\text{H}_{26}\text{Cd}_2\text{N}_8\text{O}_8\text{S}_2$ (%): C, 36.0; H, 3.2; N, 12.9; S, 7.4. Found (%): C, 36.0; H, 3.4; N, 12.7; S, 7.2. IR (KBr, cm^{-1}): 3,432(w), 1,603(w), 1,567(w), 1,414(w), 1,288(s),

1,220(w), 1,183(m), 1,075(m), 1,046(w), 1,007(s), 807(m), 630(m).

Synthesis of complex 2

The synthesis of colorless block crystals of **2** followed the same procedure as for **1**, except that $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was replaced by $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Yield: 50 %. Anal. Calc. for $\text{C}_{54}\text{H}_{60}\text{Cd}_2\text{N}_{18}\text{O}_{14}\text{S}_4$ (%): C, 42.2; H, 3.9; N, 13.7; S, 8.3. Found (%): C, 42.3; H, 3.8; N, 13.4; S, 8.5. IR (KBr, cm^{-1}): 3,391(m), 1,601(w), 1,532(s), 1,490(s), 1,411(w), 1,399(m), 1,371(s), 1,355(m), 1,271(w), 1,249(m), 1,226(w), 1,180(w), 1,047(w), 1,006(s), 806(w), 629(m).

Synthesis of complex 3

The preparation of **3** was similar to **1**, but using Na_2mtms (120.6 mg, 0.5 mmol), $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (372.4 mg, 1 mmol), H_2O (10 mL), CH_3OH (5 mL), and bpy (155.6 mg, 1 mmol). After 3 days, pale yellow block crystals were obtained. Yield: 55 %. Anal. Calc. for $\text{C}_{33}\text{H}_{35}\text{ClN}_{10}\text{O}_{11}\text{S}_2\text{Zn}_2$ (%): C, 40.5; H, 3.6; N, 14.3; S, 6.6. Found (%): C, 40.4; H, 3.9; N, 14.2; S, 6.4. IR (KBr, cm^{-1}): 3,427(w), 1,611(w), 1,596(w), 1,535(m), 1,489(s), 1,416(w), 1,389(m), 1,319(s), 1,216(w), 1,187(w), 1,105(w), 1,046(w), 1,016(m), 807(w), 642(m).

Synthesis of complex 4

Complex **4** was prepared by a similar procedure as described for **1**, using Na_2mtms (120.6 mg, 0.5 mmol), $\text{Co}(\text{N}-\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$ (145.5 mg, 0.5 mmol), bpy (155.5 mg, 1 mmol), 15 ml (2:1) $\text{H}_2\text{O}/\text{EtOH}$, and five drops of DMF. Red block crystals were obtained after 14 days. Yield: 61 %. Anal. Calc. for $\text{C}_{34}\text{H}_{48}\text{Co}_2\text{N}_{14}\text{O}_{16}\text{S}_4$ (%): C, 35.4; H, 4.2; N, 17.0; S, 11.1. Found (%): C, 35.1; H, 4.2; N, 17.1; S, 11.4. IR (KBr, cm^{-1}): 3,411(w), 1,656(m), 1,629(m), 1,535(s), 1,492(s), 1,413(w), 1,390(s), 1,373(m), 1,293(m), 1,259(s), 1,238(w), 1,189(w), 1,068(m), 1,043(w), 813(m), 629(m).

X-ray crystallography

Diffraction data were collected on a Bruker Smart CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298 K. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL-97 [23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined by a riding mode. The crystallographic data for **1–4** are listed in Table 1. Selected bond lengths and angles are listed in Table 2 \dagger in the Supplementary Information.

Results and discussion

Crystal structure of complex 1

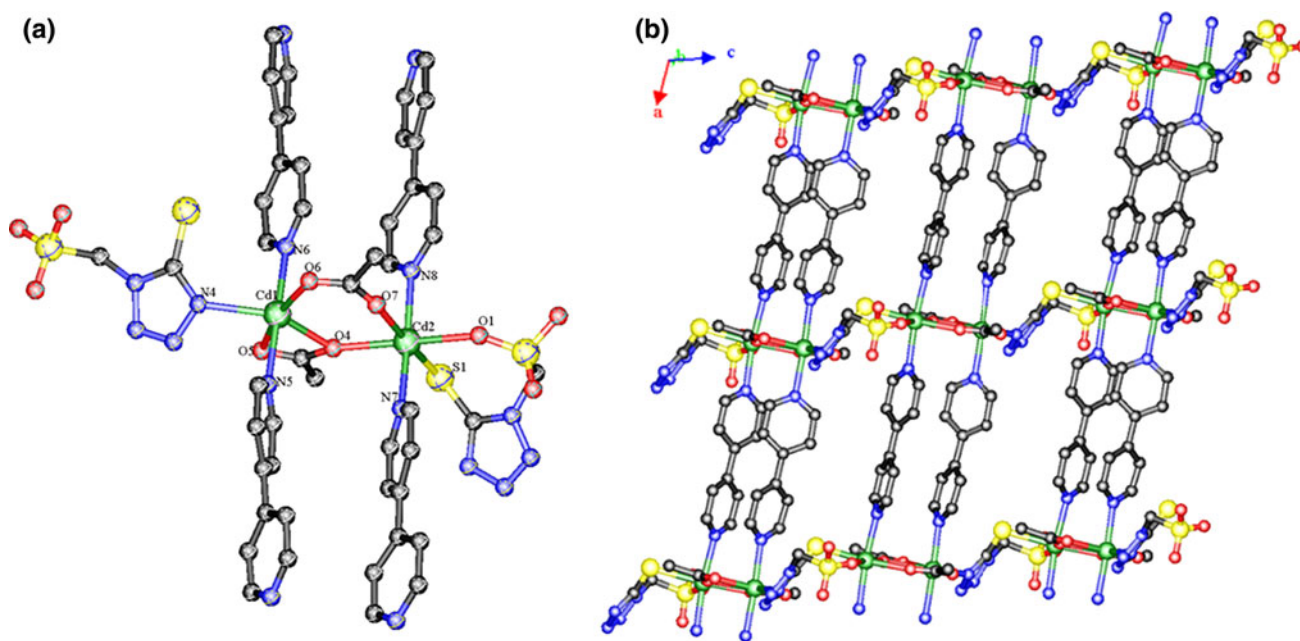
As shown in Fig. 1a, complex **1** exhibits a dimeric structure in which two Cd atoms are bridged by two acetates; one adopts *syn-syn* mode (μ_2, η^2 -carboxylato), and the other coordinates through one O atom (μ_2, η^1 -carboxylato), which is different to other previously reported binuclear Cd(II) complexes [24]. The Cd \cdots Cd distance is 3.9462 \AA . Cd1 and Cd2 adopt octahedral coordination geometries. Cd1 is coordinated by three O atoms from two acetates, and three N atoms from two bpy ligands and one mtms ligand. Cd2 is ligated by two N atoms from two bpy ligands, two O atoms from two acetate anions, plus one O atom and one S atom from an mtms ligand. The mtms acts as a tridentate-bridging ligand (Scheme 1, mode I) to link adjacent dimeric Cd(II) units, generating a 1D zigzag infinite chain. The adjacent Cd-mtms chains are further connected into a 2D pillared-layer architecture by bridging-bpy ligands along the *ac* plane (Scheme 2, mode I) (Fig. 1b). Finally, complex **1** forms a supramolecular 3D network through intermolecular hydrogen bonds [$\text{O}8\cdots\text{O}6 = 2.848(16) \text{ \AA}$, $\text{O}8\cdots\text{H}8\text{B}\cdots\text{O}2\text{A} = 2.788(19) \text{ \AA}$] (symmetry code: $A: x + 1/2, -y + 3/2, z + 1/2$) (Fig. 1c \dagger). The relevant hydrogen bond parameters are summarized in Table 3 \dagger .

Crystal structure of complex 2

Complex **2** was synthesized in a similar way as for **1**, except that $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was replaced by $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. However, complex **2** shows a linear, infinite 1D polymeric structure with a neutral component $[\text{Cd}(\text{mtms})(\text{bpy})_2(\text{H}_2\text{O})_2]$ as the repeating unit (Fig. 2a), which is quite different from complex **1**. The Cd atom is in a distorted octahedral geometry, with three N atoms from three bpy ligands, two O atoms from two coordinated water ligands, and one S atom from an mtms ligand. The mtms ligand adopts an S-bonding monodentate coordination mode (Scheme 1, mode II), and the tetrazole ring is on the outside, as also found in our previously reported mercapto-tetrazole complexes $[\text{Cd}(\text{mtz})_2\text{Br}_2]$ (mtz = 1-[2-(*N,N*-dimethylamino-ethyl)-5-mercapto-1H-tetrazole] [8] and $\{[\text{Co}^{\text{III}}(\text{mmtz})_2(1,10\text{-phen})_2]\cdot\text{NO}_3\}$ (mmtz = 1-methyl-5-mercapto-tetrazole [14]. Of the bpy ligands in complex **2**, one adopts a terminal coordination mode to link Cd(II) forming $[\text{CdN}_3\text{O}_2\text{S}]$ units (Scheme 2, mode II), while the other acts as a spacer to bridge the $[\text{CdN}_3\text{O}_2\text{S}]$ units, leading to 1D infinite chains along the *b* axis (Scheme 2, mode I). These 1D chains are further connected into a 3D supramolecular framework through π - π stacking interactions from the free neutral bpy ligands (Scheme 2, mode V) and hydrogen bonds among the bpy ligands (Scheme 2,

Table 1 Crystal data and structure refinement summary for complexes 1–4

Complex	1	2	3	4
Empirical formula	C ₂₆ H ₂₆ Cd ₂ N ₈ O ₈ S ₂	C ₅₄ H ₆₀ Cd ₂ N ₁₈ O ₁₄ S ₄	C ₃₃ H ₃₅ ClN ₁₀ O ₁₁ S ₂ Zn ₂	C ₃₄ H ₄₈ Co ₂ N ₁₄ O ₁₆ S ₄
Formula weight	867.51	1,538.24	978.02	1,155.00
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>Cc</i>	<i>Cc</i>	<i>P2(1)/c</i>	<i>P-1</i>
<i>a</i> (Å)	11.7124(12)	24.426(3)	14.7772(12)	10.1567(11)
<i>b</i> (Å)	16.6543(15)	11.90640(13)	10.4334(19)	11.5085(12)
<i>c</i> (Å)	17.160(2)	24.025(3)	26.390(3)	12.2008(15)
α (°)	90.00	90.00	90.00	111.215(2)
β (°)	107.439(2)	115.269(2)	95.004(2)	102.207(1)
γ (°)	90.00	90.00	90.00	99.766(1)
Volume (Å ³)	3,193.4(6)	6,318.5(10)	4,053.2(9)	1,251.1(2)
<i>Z</i>	4	4	4	1
Calculated density (Mg/m ³)	1.804	1.617	1.603	1.533
Reflections collected	8,001	15,916	19,921	6,510
Independent reflections	5,621 [<i>R</i> (int) = 0.056]	8,743 [<i>R</i> (int) = 0.0340]	7,143 [<i>R</i> (int) = 0.0476]	4,413 [<i>R</i> (int) = 0.054]
Data/restraints/parameters	4,881/9/417	8,743/2/830	7,143/0/590	4,299/3/319
Goodness of fit on <i>F</i> ²	1.03	1.055	1.017	1.00
Final <i>R</i> indices [<i>I</i> > 2(<i>I</i>)]	<i>R</i> ₁ = 0.0593 <i>wR</i> ₂ = 0.1031	<i>R</i> ₁ = 0.0345, <i>wR</i> ₂ = 0.0700	<i>R</i> ₁ = 0.0450, <i>wR</i> ₂ = 0.0977	<i>R</i> ₁ = 0.0737, <i>wR</i> ₂ = 0.1733
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0915, <i>wR</i> ₂ = 0.1122	<i>R</i> ₁ = 0.0487, <i>wR</i> ₂ = 0.0780	<i>R</i> ₁ = 0.0915, <i>wR</i> ₂ = 0.1233	<i>R</i> ₁ = 0.1229, <i>wR</i> ₂ = 0.1994

**Fig. 1** **a** View of the coordination environment of the Cd(II) center in **1**. Symmetry codes: *A*: $x, -y + 1, z + 1/2$. **b** View of the 2D pillared-layer of **1** along the *ac* plane. Symmetry code: (*A*) $x + 1/2, -y + 3/2, z + 1/2$

mode III, IV), coordinated water, and the uncoordinated O atom of the mtms ligand (Fig. 2b†). In short, the bpy ligands play an important role in forming the structure of **2**, revealing five different coordination modes.

Crystal structure of complex **3**

Use of Zn(ClO₄)₂·6H₂O instead of Cd(ClO₄)₂·6H₂O gave complex **3**, whose structure with *P2(1)/c* space group is

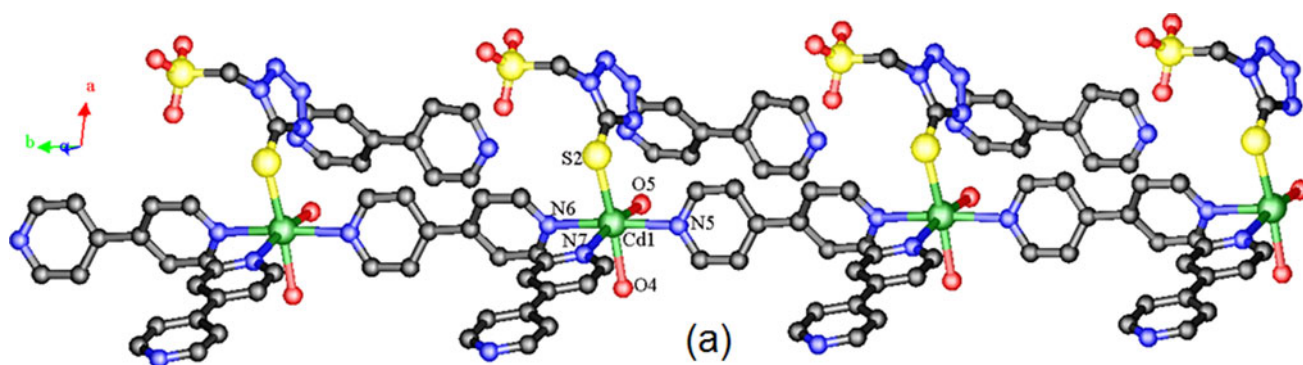


Fig. 2 a View of the 1D infinite chain of **2** along the *b* axis. Symmetry codes: A: $x, y - 1, z$

different from that of complex **2**. In complex **3** (Fig. 3a), the bidentate-bridging mtms ligand (Scheme 1, mode III) combines with an μ_2 -OH bridge between two Zn atoms to form a binuclear unit. The coordination environment of **3** shows a butterfly-like structure, in which four bpy ligands act as the wings, while the mtms ligand is located at the head. Zn1 is surrounded by two bpy ligands, one mtms ligand, one coordinated water ligand, and one hydroxy ligand to form a distorted trigonal-bipyramidal geometry. The axial positions are occupied by N4 and O5 with an N4–Zn1–O5 bond angle of $174.12(13)^\circ$. While Zn2 is in a distorted tetrahedral coordination geometry provided by one hydroxy, one mtms, and two bpy ligands. The Zn–N bond distances range from 2.022(4) to 2.215(4) Å, and the Zn–S bond distance is 2.3215(16) Å, which are similar to other complexes [23, 24]. The binuclear units link each other by bpy ligands (Scheme 2, mode I, II) to form a 1D zigzag chain along the *c* axis. The most important inter-chain interaction in the crystal packing is hydrogen bonds among uncoordinated ClO_4^- , coordinated hydroxy, coordinated water, free water, the uncoordinated sulfonic group of mtms, and the bpy ligand (Scheme 2, mode III) (Fig. 3b†). Compared to the similar coordination modes of bpy in complexes **2** and **3**, the architecture of **3** is more complicated. The tetrazolyl-N of mtms can provide potential coordination sites, and uncoordinated ClO_4^- anion may also help to determine the final coordination architectures.

Crystal structure of complex 4

As illustrated in Fig. 4a, complex **4** contains two components, namely $[\text{Co}(\text{mtms})_2(\text{bpy})(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Co}(\text{bpy})_2(\text{H}_2\text{O})_4]^{2+}$ ions. Atom Co1 is located on a crystallographic inversion center and octahedrally coordinated by two mtms N atoms and two bpy N atoms in the equatorial plane, plus two coordinated water ligands in the axial positions, with an O4–Co1–O4A bond angle of

180.0° . The coordination environment of Co2 is provided by two bpy N atoms in the axial positions, with four coordinated water ligands in the equatorial plane. The Co2–N bond distances range from 2.179(6) to 2.203(5) Å, which are comparable with other complexes [25].

The structure of the complex anion $[\text{Co}(\text{mtms})_2(\text{bpy})(\text{H}_2\text{O})_2]^{2-}$ is the same as that of our previously reported complex $[\text{Co}^{\text{II}}(\text{mmtz})_2(4,4'\text{-bpy})(\text{H}_2\text{O})_2]_n$ (mmtz = 1-methyl-5-mercapto-tetrazole) [14]. The mtms acts as a N-bonding monodentate ligand (Scheme 1, mode IV). The bpy spacers bridge adjacent Co1 atoms to generate a 1D chain along the *b* axis (Scheme 2, mode II). The bpy ligands adopt terminal coordination mode (Scheme 2, mode I) to link Co2 centers, forming the cationic complex $[\text{Co}(\text{bpy})_2(\text{H}_2\text{O})_4]^{2+}$. These Co2 components are vertically penetrating into the 1D chains of Co1, showing a rail-like structure (Fig. 4d). The supramolecular structure mainly depends on the π - π stacking of bpy (Scheme 2, mode V), and intermolecular hydrogen bonds among the water ligands, the uncoordinated sulfonic group of the mtms ligand, and the bpy ligand (Scheme 2, mode III).

Photoluminescence properties

It is well known that Cd(II) complexes can exhibit interesting luminescence properties [8, 24]. The solid-state luminescence of the free Na_2mtms ligand and complexes **1** and **2** was investigated at room temperature and is shown in Fig. 5†. Na_2mtms shows an emission peak at 460 nm when excited at 301 nm. Upon excitation at 304 nm, complexes **1** and **2** display emission maxima at 353 and 362 nm, respectively, which are both greatly blue-shifted compared to the free Na_2mtms ligand. Since the Cd(II) center has d^{10} electronic configuration, the emissions of complexes **1** and **2** can be tentatively assigned to ligand-to-metal charge transfer (LMCT) [26–28]. These complexes may be suitable as blue-light-emitting materials, since they show luminescence in the blue region [29].

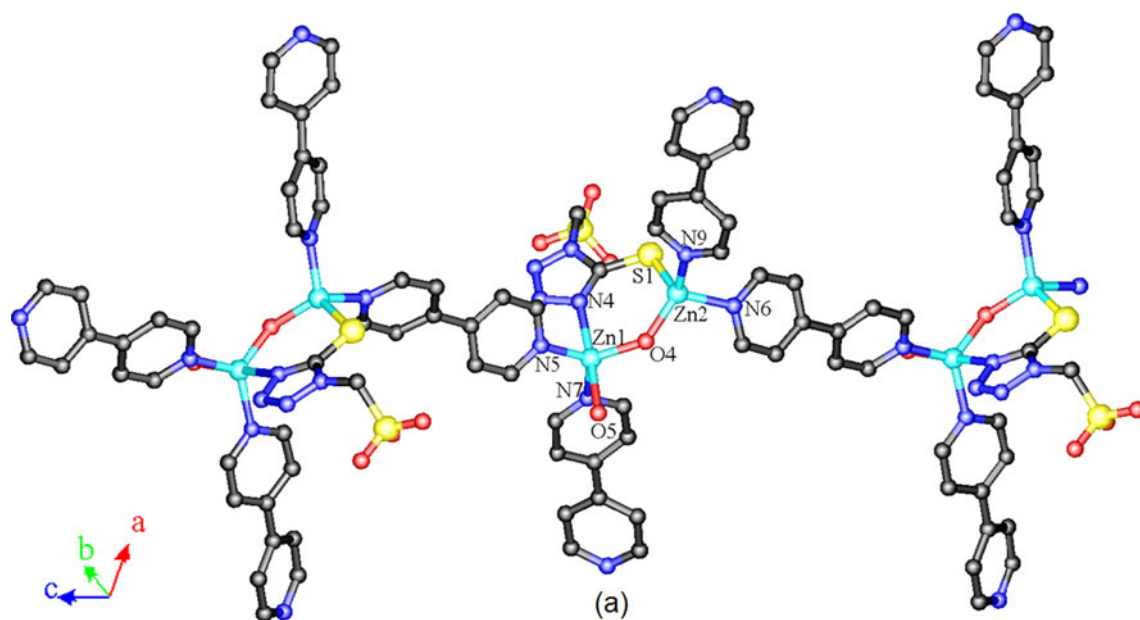


Fig. 3 **a** 1D infinite chain of 3 along the *c* axis. Symmetry codes: (A) $x, y - 1, z$; (B) $x + 1, y, z$; (C) $-x + 1, y + 1/2, -z + 5/2$

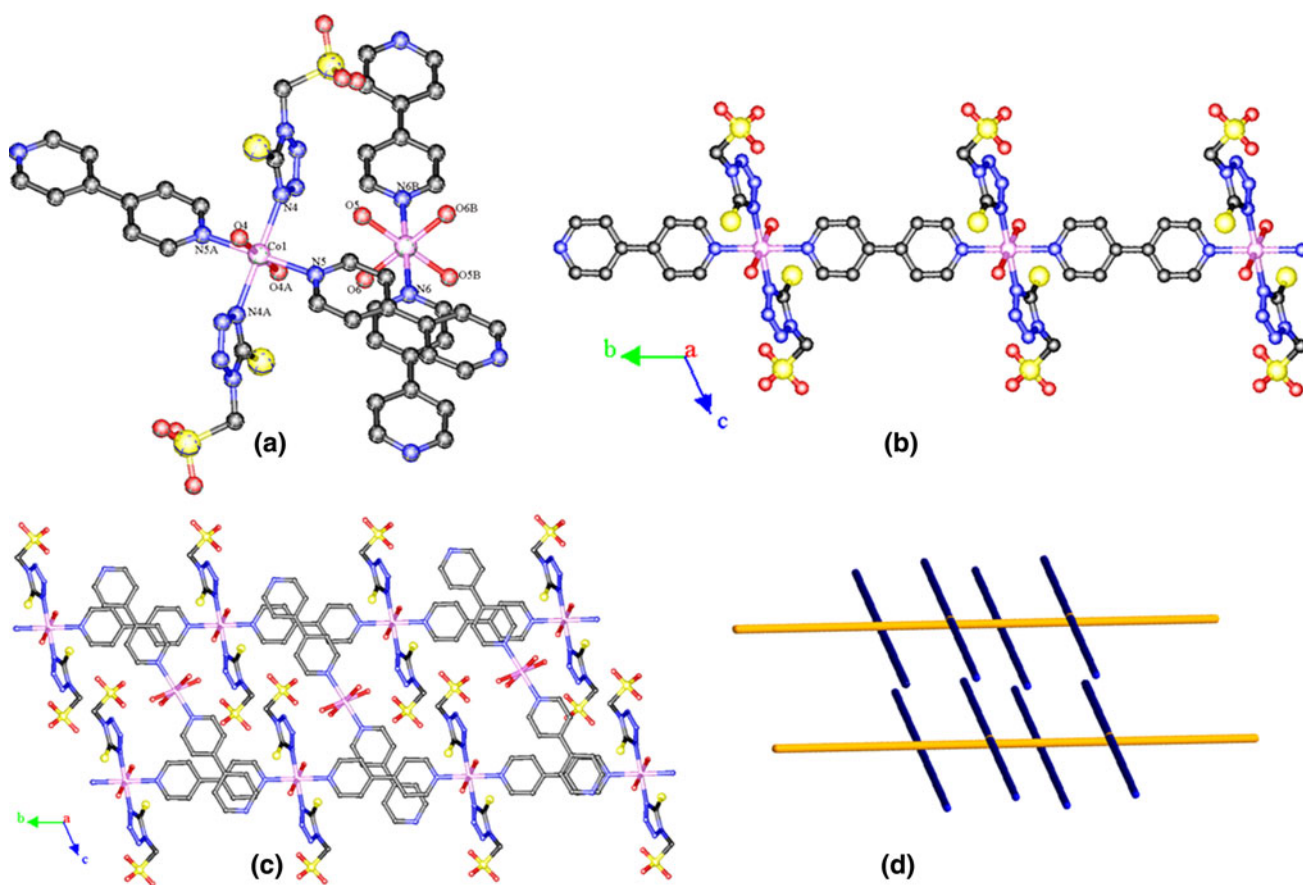


Fig. 4 **a** View of the coordination environment of the Co(II) center in **4**. Symmetry codes: A: $-x + 1, -y + 1, -z$; B: $-x + 2, -y, -z + 1$. **b** View of the 1D infinite chain of Co1 along the *b* axis. **c** Stacked plot of **4** with the 1D chains of Co1 and free Co2 units. **d** A

schematic illustration of the packing of **4**. Symmetry codes: (A) $-x + 1, -y + 1, -z$; (B) $x, y - 1, z$; (C) $-x + 2, -y, -z$; (D) $x + 1, y - 1, z$; (E) $x + 1, y, z$; (F) $-x + 1, -y + 1, -z + 1$; (G) $x, y + 1, z$; (H) $-x + 1, -y + 2, -z + 1$

Cyclic voltammetry

The cyclic voltammogram of **3** was measured with a conventional three-electrode cell in aqueous solution with complex concentration of $1.0 \times 10^{-5} \text{ mol L}^{-1}$, as shown in Fig. 6†. Measurements were carried out at room temperature by scanning from -0.600 to $+1.400 \text{ V}$ at different scan rates. The CV shows an oxidation peak at 0.444 V with the scan rate of 50 mV s^{-1} , while there is no corresponding reduction wave. As the scan rate is increased to 80 and 100 mV s^{-1} , the anodic peak appears at 0.479 and 0.567 V , respectively. Again, no corresponding cathodic wave was observed, showing that the electrochemical behavior of the Zn(II)/Zn(I) redox couple is irreversible [30].

Conclusion

Four new complexes have been constructed from mixed mtms and bpy ligands. The 2D pillared-layer structure of **1** is obtained with carboxylato groups, while complexes **2**, **3**, and the host structure **4** all exhibit 1D infinite chain structures. The results demonstrate that coordinated anions can increase the dimensionality of the crystal structures, while uncoordinated anions can propagate the architectures through hydrogen bonding and π - π stacking interactions. The mtms ligand shows four different coordination modes in the four complexes. The varied coordination modes of the neutral rigid linear bpy ligand (bridging coordination, terminal coordination, hydrogen bond, and π - π stacking) found in this study proves that it is an excellent building block in constructing novel hybrid frameworks. In summary, for the complexes **1–4** described in this paper, we can see that the properties of the anion, mtms, and bpy ligands all help to determine the final coordination architectures.

Supplementary Information

CCDC 929454–929457 contain the supplementary crystallographic data for complexes **1–4**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments We gratefully acknowledge the National Nature Science Foundation of China (Nos. 21101035 and 21061002), Guangxi Natural Science Foundation of China (2010GXNSFF 013001, 2012GXNSFAA053035, and 2012GXNSFBA053017), the Foundation of Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources (CMEMR2011-20), and the Nature Science Foundation of Guangxi Normal University.

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