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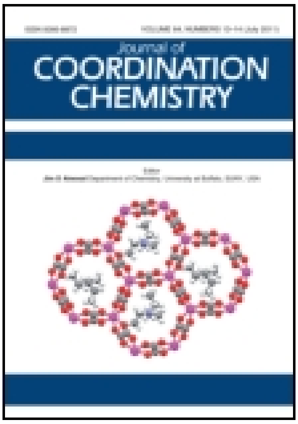

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Synthesis, crystal structures, and fluorescence properties of transition metal complexes derived from an unsymmetrical N-heterocyclic ligand

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Synthesis, crystal structures, and fluorescence properties of transition metal complexes derived from an unsymmetrical N-heterocyclic ligand

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Four transition metal complexes, $[Mn(Hbimtz)_2(H_2O)_2(NCS)_2]$ (**1**), $[Co(Hbimtz)_2(H_2O)_2(NCS)_2]$ (**2**), $[Pb(Hbimtz)Br_2]_n$ (**3**), and $\{[Ag_2(Hbimtz)_3]SO_4 \cdot 4H_2O\}_n$ (**4**) (Hbimtz = 1-[(1H-benzimidazol-2-yl)-methyl]-1,2,3,4-tetrazole), were synthesized and characterized by single-crystal X-ray diffraction. The Mn(II) of **1** and Co(II) of **2** are six-coordinate with two nitrogen atoms from Hbimtz, two nitrogen atoms from thiocyanate and two water molecules. The geometry of Pb(II) in **3** is a distorted octahedron with two nitrogen atoms of two Hbimtz's and four Br^- ions, including the weak bond between the Pb1 and N6 of Hbimtz. Complex **3** is assembled into a 1-D $[PbBr_2]_n$ inorganic chain by μ_2-Br^- and into a 2-D layer by weak interactions. The Ag(II) of **4** has two geometries, linear and tetrahedral. Hbimtz bridges the two kinds of Ag(II) into a 1-D helical chain. Fluorescence of **3** and **4** were also investigated.

Keywords: Crystal structure; 1-[(1H-benzimidazol-2-yl)-methyl]-1,2,3,4-tetrazole; Transition metal complexes; Photoluminescence properties

1. Introduction

Tetrazole compounds have been studied for 100 years and have many applications. Some applications of polyazaheteroaromatic compounds as donors give the possibility to tune the properties of the organic ligands by careful selection of the polyazole donors or by changing the types and positions of the substituents in the five-membered ring [1–6]. Among polyazaheteroaromatic compounds, tetrazole and its derivatives are very interesting ligands because they combine the possible bridging of pyrazoles (N1, N2–), imidazoles (N1, N3–), 1,2,3-triazoles (N1, N2, N3–), and 1,2,4-triazoles (N1, N2, N4–) with regard to the arrangement of their four nitrogen atoms (scheme 1).

Benzimidazolyl normally forms coordination bonds through its amino nitrogen and the amino nitrogen serves as a potential hydrogen bond donor [7–10].

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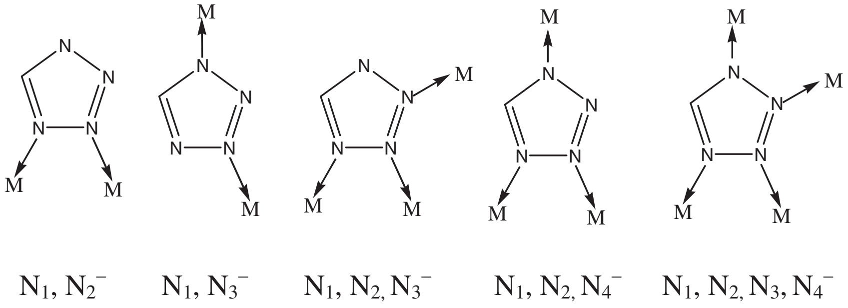


Scheme 1. Bridging fashions of tetrazole.

Therefore, coordinations based on benzimidazolyl produces supramolecular polymers incorporating both coordination and non-classical intermolecular interactions.

We have synthesized 1-[(1H-benzimidazol-2-yl)-methyl]-1,2,3,4-tetrazole (Hbimtz) from tetrazole-1-acetic acid and 1,2-phenylenediamine by cyclization. In previous research, Hou and coworkers studied the influence of the anion on the coordination mode of Cd(II) complexes with Hbimtz [11]. Herein, we explore the structures and fluorescence properties of four other transition metal complexes with Hbimtz.

2. Experimental

2.1. *Materials and instruments*

All reagents and solvents employed were commercially available and used without purification. 1-[(1H-benzimidazol-2-yl)-methyl]-1,2,3,4-tetrazole (Hbimtz) was synthesized from 1,2-phenylenediamine, polyphosphoric acid and 1,2,3,4-tetrazole acetic acid according to literature methods, similar to Phillip's method [12, 13].

Elemental analyses for C, H, and N were carried out on a Model 2400 II Perkin-Elmer elemental analyzer. IR spectra were taken on a Perkin-Elmer Spectrum One FT-IR spectrometer from 4000 to 400 cm^{-1} using KBr pellets. Fluorescence measurements were performed using a Hitachi F-4500 spectrofluorimeter at ambient temperature in the solid state.

2.2. *Synthesis*

2.2.1. Preparation of [Mn(Hbimtz)$_2$(H$_2$O)$_2$(NCS)$_2$] (1). Hbimtz (0.12 g, 0.6 mmol) was dissolved in acetonitrile solution (5 mL) and a solution of Mn(NO$_3$)$_2$ (0.054 g, 0.3 mmol) in H_2O (5 mL) was added dropwise. Then potassium thiocyanate (0.019 g, 0.2 mmol) was added to the mixture. The final mixture was stirred at room temperature for 3.5 h and filtered. The filtrate was allowed to slowly concentrate by evaporation at room temperature. After 2 weeks, colorless crystals were obtained and washed with ethanol. Yield 55%, based on Mn. Anal. Calcd for $C_{20}H_{20}MnN_{14}O_2S_2$: C, 39.54; H, 3.32; N, 32.28. Found: C, 39.51; H, 3.30; N, 32.31. IR (solid KBr pellet/cm^{-1}): 3416(m), 3198(br), 2076(s), 1660(m), 1489(w), 1463(s), 1446(s), 1421(m), 1328(m), 1313(m), 1275(m), 1231(w), 1183(m), 1166(w), 1113(m), 1031(m), 1003(w), 988(m), 873(m), 855(m), 788(s), 749(s), 654(m), 639(br).

2.2.2. Preparation of [Co(Hbimtz)$_2$(H$_2$O)$_2$(NCS)$_2$] (2). The procedure followed was similar to that of **1** except that $Co(NO_3)_2 \cdot 6H_2O$ (0.087g, 0.3 mmol) was used instead of $Mn(NO_3)_2$. Pink block crystals suitable for X-ray diffraction were obtained about 2 weeks later by slow evaporation of the solvent. Yield: 65%, based on Co. Anal. Calcd for $C_{20}H_{20}CoN_{14}O_2S_2$: C, 39.28; H, 3.30; N, 32.07. Found: C, 39.24; H, 3.30; N, 32.09. IR (solid KBr pellet/cm^{-1}): 3416(m), 3201(br), 2076(s), 1660(m), 1485(w), 1465(s), 1447(s), 1421(m), 1328(m), 1313(m), 1275(m), 1231(w), 1183(m), 1166(w), 1113(m), 1031(m), 1003(w), 988(m), 873(m), 855(m), 788(s), 749(s), 654(m), 639(br).

2.2.3. Preparation of [Pb(Hbimtz)Br$_2$]$_n$ (3). Hbimtz (0.06 g, 0.3 mmol) was dissolved in ethanol solution (5 mL) and a solution of $Pb(NO_3)_2$ (0.199 g, 0.6 mmol) in H_2O (5 mL) was added dropwise. Then potassium bromide (0.222 g, 0.2 mmol) was added to the mixture. The final mixture was refluxed for 3.5 h. After slow cooling to room temperature and filtration, the filtrate was allowed to slowly concentrate by evaporation at room temperature. Two weeks later, colorless crystals were obtained and washed with water. Yield 65%, based on Pb. Anal. Calcd for $C_9H_8Br_2N_6Pb$: C, 19.06; H, 1.42; N, 14.82. Found: C, 19.10; H, 1.45; N, 14.78. IR (solid KBr pellet/cm^{-1}): 3145(w), 2994(w), 2750(br), 1591(m), 1540(m), 1477(w), 1456(s), 1447(s), 1395(s), 1337(s), 1305(m), 1275(s), 1224(m), 1165(m), 1099(s), 1033(s), 1003(w), 966(m), 867(w), 739(s), 656(w).

2.2.4. Preparation of {[Ag$_2$(Hbimtz)$_3$]SO$_4$ · 4H$_2$O}$_n$ (4). The procedure followed was similar to that of **3** except that acetonitrile solution was used instead of ethanol, Ag_2SO_4 (0.187 g, 0.6 mmol) instead of $Pb(NO_3)_2$ and sodium perchlorate (0.037 g, 0.3 mmol) instead of potassium bromide (0.222 g, 0.2 mmol). Colorless bar crystals suitable for X-ray diffraction were obtained about a month later by slow evaporation of the solvent. Yield: 55%, based on Ag. Anal. Calcd for $C_{27}H_{32}Ag_2N_{18}O_8S$: C, 32.94; H, 3.28; N, 25.61. Found: C, 32.90; H, 3.31; N, 25.64. IR (solid KBr pellet/cm^{-1}): 3186(br), 3128(s), 1624(w), 1536(w), 1462(m), 1447(br), 1339(w), 1318(w), 1280(m), 1221(w), 1141(s), 1087(br), 1035(m), 853(w), 753(s), 715(w), 662(w), 626(w).

2.3. *X-ray crystallography*

Suitable single crystals with dimensions of $0.23 \times 0.20 \times 0.16\,mm^3$ for **1**, $0.30 \times 0.20 \times 0.12\,mm^3$ for **2**, $0.21 \times 0.08 \times 0.06\,mm^3$ for **3**, and $0.32 \times 0.28 \times 0.27\,mm^3$ for **4** were carefully selected and glued to thin glass fibers with epoxy resin. Crystal structural measurements for **1**, **2**, **3**, and **4** were performed on a Bruker Smart CCD apparatus using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated positions [14, 15]. The crystal data and structure refinement results are summarized in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data for **1**–**4**.

Complexes	**1**	**2**	**3**	**4**
Formula	$C_{20}H_{20}MnN_{14}O_2S_2$	$C_{20}H_{20}CoN_{14}O_2S_2$	$C_9H_8Br_2N_6Pb$	$C_{27}H_{32}Ag_2N_{18}O_8S$
Formula weight	607.56	611.55	567.22	984.51
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$
Unit cell dimensions (Å, °)				
a	8.9690(10)	9.0230(8)	9.1017(8)	7.7002(8)
β	9.0269(12)	9.0889(9)	22.248(2)	13.6772(14)
c	9.0681(13)	9.1131(11)	7.3831(6)	17.6436(18)
α	95.8230(10)	95.8440(10)	90	89.560(2)
β	115.924(2)	115.823(2)	113.8290(10)	78.9430(10)
Γ	91.0740(10)	91.1780(10)	90	80.0390(10)
Volume (Å^3), Z	655.25(15), 1	667.47(12), 1	1367.6(2), 4	1795.6(3), 2
Calculated density (g cm^{-3})	1.540	1.521	2.755	1.821
Absorption coefficient (mm^{-1})	0.712	0.847	18.171	1.225
Reflections collected	3374	3446	6924	8968
Unique reflections	2275	2316	2414	6275
R_{int}	0.0405	0.0344	0.0656	0.0125
Data/restraints/parameters	2275/0/178	2316/0/178	2414/0/163	6275/0/533
Goodness-of-fit on F^2	1.055	1.056	1.048	1.026
R_1 [$I > 2\sigma(I)$]	0.0536	0.0631	0.0308	0.0427
wR_2 [$I > 2\sigma(I)$]	0.1174	0.1629	0.0693	0.1172
R_1 (all data)	0.0806	0.0885	0.0408	0.0494
wR_2 (all data)	0.1270	0.1838	0.0725	0.1246

Table 2. Selected bond distances (Å) and angles (°) for **1**–**4**.

Complex **1**			
Mn(1)–N(7)	2.170(3)	N(7)–Mn(1)–N(1)	89.51(12)
Mn(1)–O(1)	2.198(2)	O(1)–Mn(1)–N(1)	87.82(10)
Mn(1)–N(1)	2.305(3)	N(7)–Mn(1)–O(1)	94.03(11)
Complex **2**			
Co(1)–N(7)	2.182(4)	N(7)–Co(1)–N(1)	90.46(14)
Co(1)–O(1)	2.211(3)	O(1)–Co(1)–N(1)	92.08(12)
Co(1)–N(1)	2.320(4)	N(7)–Co(1)–O(1)	94.01(13)
Complex **3**			
Pb(1)–N(1)	2.623(6)	N(1)–Pb(1)–Br(2)	93.01(11)
Pb(1)–Br(1)A	2.9178(9)	N(1)–Pb(1)–Br(1)A	92.74(13)
Pb(1)–Br(2)B	3.1253(9)	Br(2)–Pb(1)–Br(1)A	90.53(2)
Pb(1)–Br(2)	2.8744(8)	Br(1)A–Pb(1)–Br(1)	92.62(2)
Pb(1)–Br(1)	3.0915(9)	N(1)–Pb(1)–Br(2)B	93.91(12)
		Br(2)–Pb(1)–Br(2)B	79.18(2)
N(1)–Pb(1)–Br(1)	167.57(12)	Br(1)A–Pb(1)–Br(2)B	168.02(2)
Br(2)–Pb(1)–Br(1)	98.14(3)	Br(1)–Pb(1)–Br(2)B	82.88(2)
Complex **4**			
Ag(1)–N(1)	2.097(3)	N(1)–Ag(1)–N(7)	95.94(15)
Ag(1)–N(7)	2.100(3)	N(13)–Ag(2)–N(18)A	175.03(13)
Ag(2)–N(13)	2.234(4)	N(13)–Ag(2)–N(5)	107.52(14)
Ag(2)–N(18)A	2.359(4)	N(18)A–Ag(2)–N(5)	120.46(15)
Ag(2)–N(12)	2.301(4)	N(13)–Ag(2)–N(12)	120.34(14)
Ag(2)–N(5)	2.549(4)	N(12)–Ag(2)–N(18)A	122.66(14)
		N(12)–Ag(2)–N(5)	86.11(14)

Symmetry codes: For **3**: A: x, $1/2-y$, $1/2+z$; B: x, $1/2-y$, $-1/2+z$; for **4**: A: $x-1$, y, z

3. Results and discussion

3.1. *Structural description of [Mn(Hbimtz)$_2$(H$_2$O)$_2$(NCS)$_2$] (1)*

X-ray crystallographic analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$. Figure 1(a) depicts the coordination geometry of the Mn(II) center. The structure is built from a centrosymmetric unit, the asymmetric unit contains half of the manganese, one thiocyanate, one water molecule and one Hbimtz. In [Mn(Hbimtz)$_2$(H$_2$O)$_2$(NCS)$_2$], Mn(II) is coordinated to two Hbimtz [Mn1–N1 2.305(3) Å], two nitrogen atoms from thiocyanate [Mn1–N7 2.170(3) Å] and two water molecules [Mn1–O1 2.198(2) Å], respectively, forming an elongated octahedron. Two thiocyanate nitrogen atoms (N7, N7A) and two water molecules (O1, O1A) reside in the equatorial plane, while two benzimidazolyl nitrogen atoms (N1, N1A) occupy the axial positions. Hbimtz is monodentate (scheme 2, mode I) and the dihedral angle between the planes through coordinated benzimidazole and the non-coordinated tetrazole is 95.6°, larger than that of the free ligand (81.5°) [11].

The most interesting aspect of the structure is the way in which mononuclear units are interlinked *via* hydrogen bonds (table 3) into a 3-D network. In **1**, offset face-to-face π-stacking interaction is found between inter-molecular benzimidazolyl rings (figure 1b). The inter-planar separations between rings at benzimidazole (x, y, z) and benzimidazole $(1-x, -y, 1-z)$ is 3.423 Å, and the center-to center separations are 3.572(3) Å, in the range of distances for $\pi\cdots\pi$ interactions between two aryl rings [16].

3.2. *Structural description of [Co(Hbimtz)$_2$(H$_2$O)$_2$(NCS)$_2$] (2)*

Complex **2** is isomorphous with **1** (figure 2a). The main difference between **1** and **2** lies in the coordination geometry of the metal ions. In **2**, the octahedral geometry is only slightly elongated along the axes defined by the two benzimidazolyl nitrogen atoms [Co1–N7 2.182(4) Å, Co1–N1 2.320(4) Å, Co–O1 2.211(3) Å], which are close to [Co(HL)$_2$(Py)$_2$(H$_2$O)$_2$] ($H_2L = $ 1-(4-hydroxyphenyl)-5-mercaptotetrazole) [17] and trichloro[(1*H*-benzimidazol-2-ylmethyl)-(ethyl)ammonium-N^3]cobalt(II) [18].

There also exist offset $\pi\cdots\pi$ stacking interactions in **2** (figure 2b). The separation and centroid distances between the two adjacent benzimidazolyl rings are 3.444 and 3.582 Å, respectively. Hydrogen-bonding interactions (table 4) extend into a 3-D supramolecular framework.

3.3. *Structural description of [Pb(Hbimtz)Br$_2$]$_n$ (3)*

The crystal structure of **3** consists of neutral Pb(Hbimtz)Br$_2$ units, bridged by Br$^-$ to yield a 1-D zigzag chain with Pb$\cdots$Pb separation of 4.321 Å and dihedral angle between adjacent tetra-membered rings of 61.5° (figure 3a and b). Each Pb(II) is five-coordinate with a PbNBr$_4$ chromophore. The trigonality index τ ($\tau = (\phi_1 - \phi_2)/60$, where ϕ_1 and ϕ_2 are the two largest L–M–L angles of the coordination sphere) for Pb(II), 0.0075 confers an approximate square pyramid to the Pb(II) site ($\tau = 0$ infers a perfect square pyramid and $\tau = 1$ a perfect trigonal bipyramid). One bridging Br2 locates in the apical site. The bond distances between Pb1 and the bridging bromides range from 2.8744(8) to 3.1253(9) Å, close to the separations between 2.916(1) and 3.313(1) Å

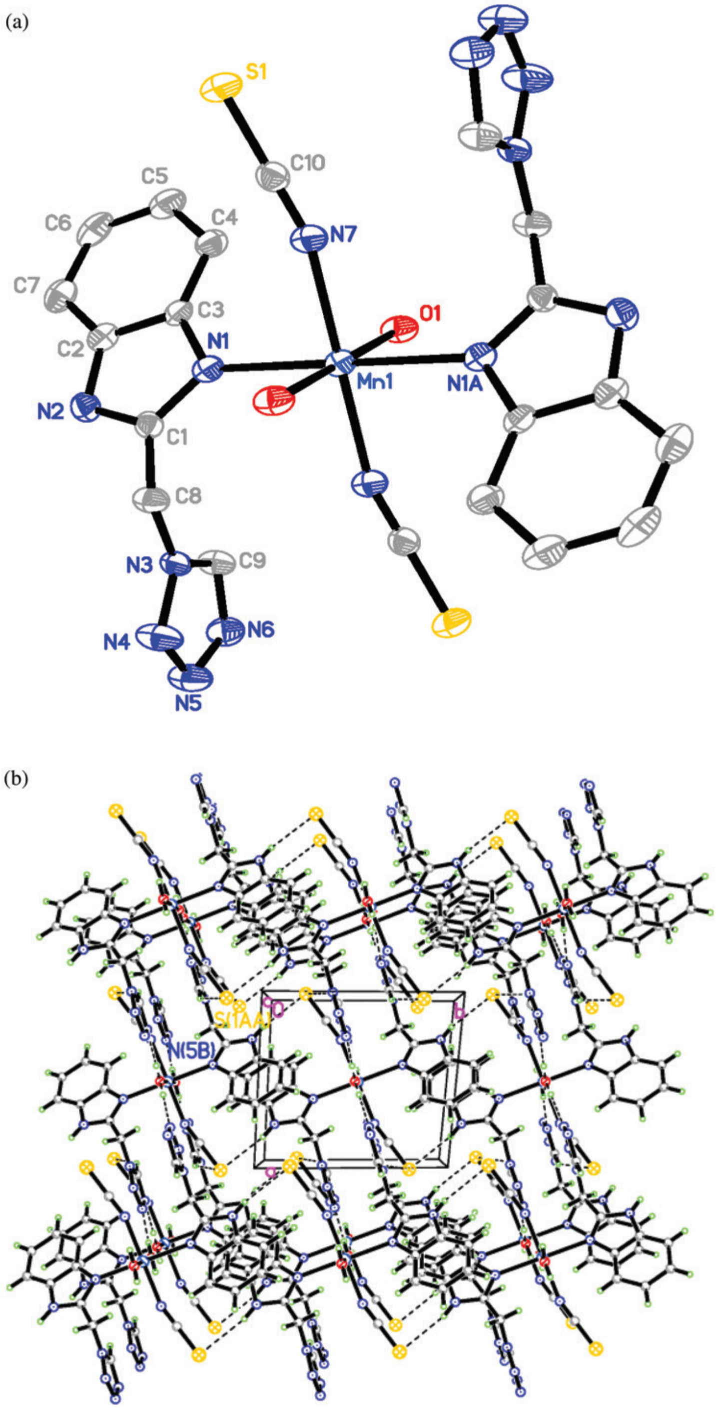
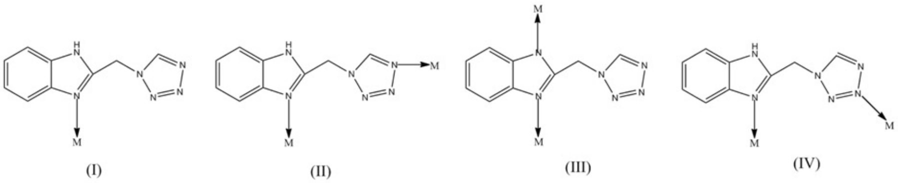


Figure 1. (a) The coordination environment of Mn(II), showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry code: A $-x+1$, $-y+1$, $-z+1$. (b) 3-D supramolecular network for **1** formed by hydrogen bonds and $\pi \cdots \pi$ interactions.



Scheme 2. Coordination modes of Hbimtz.

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

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O1–H1C···N5[i]	0.85	2.05	2.898(5)	179
O1–H1D···N6[ii]	0.85	1.96	2.813(5)	179
N2–H2···S1[iii]	0.86	2.58	3.412(4)	163
C8–H8A···O1[iv]	0.97	2.54	3.387(6)	146

Symmetry codes: [i]: $-1+x$, y, $-1+z$; [ii]: $2-x$, $1-y$, $1-z$; [iii]: $1-x$, $-y$, $1-z$; [iv]: $1-x$, $1-y$, $1-z$.

reported in the literature [19]. The Pb1–N1 bond distance is 2.623(6) Å, within the range of typical values (2.396–2.776 Å) [20]. In addition, the distance of 2.893(4) Å between Pb1 and N6C indicates some weak interaction [21], which may be viewed as a weak coordination mode. Thus, the environment of the Pb(II) atom can also be described as a distorted octahedron. The equatorial plane contains Br1, Br1A, Br2B, and N1, while the axial positions are Br2 and N6 from another chain (figure 3a). As complexes **1** and **2**, the Hbimtz in **3** coordinates monodentate to Pb(II) (scheme 2, mode II) with a dihedral angle of 65.0° between the benzimidazole and tetrazolate rings. When the weak interactions are considered, the 1-D zigzag chains are linked into 2-D wave layer *via* bridging Hbimtz (figure 3c).

3.4. *Structural description of [$Ag_2(Hbimtz)_3]SO_4\cdot 4H_2O$ (4)*

Complex **4** consists of $[Ag_2(Hbimtz)_3]^{2+}$ cations, SO_4^{2-}, and water. Figure 4(a) shows the ORTEP projection of $[Ag_2(Hbimtz)_3]^{2+}$. Two kinds of silver ions are crystallographically distinguishable. Ag1 has a linear two-coordinate structure with a N1–Ag1–N7 bond angle of 175.03(13)°. By a bridging ligand, the tetrahedral Ag2 structure is filled with other tetrazolyl N atoms (N5, N2, and N18A) and a benzimidazolyl, N3 from four Hbimtz ligands. The distances Ag1···Ag2, Ag1···Ag2A, Ag2···Ag2A, and Ag2···Ag2B are 6.782, 7.537, 7.000, and 7.000 Å, respectively. The bond lengths of Ag1–N (2.097(3)–2.100(3) Å) agree with those in $\{[Ag_2L_2][X]_2$ L = 1,3-bis(benzimidazol-1-ylmethyl)benzene), X = $CF_3SO_3^-\}$ (Ag(1)–N(1) = 2.095(5) Å) [22]; the bond lengths of Ag2–N (2.234(4)–2.549(4) Å) are slightly longer than those in $[\{Ag_2[\mu\text{-}CH(pz)_2(CH_2)_2CH(pz)_2]_3\}(NO_3)_2$ L = 1,1,4,4-tetra(1-pyrazolyl)butane] (Ag(1)–N(11) = 2.247–2.509 Å) [23].

Different from **1**, **2**, **3**, or Meng [11], there are two kinds of independent Hbimtz ligands. One with dihedral angles of 108.5° and 65.5° between the benzimidazole and

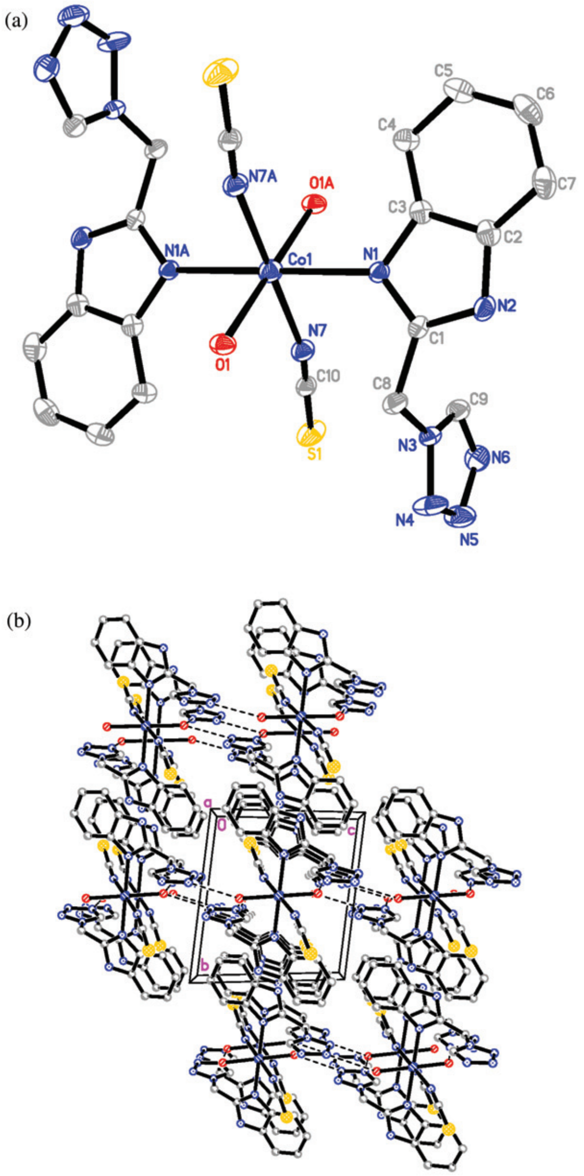


Figure 2. (a) The coordination environment of Co(II), showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Symmetry code: A: $-x+1, -y+1, -z+1$. (b) 3-D supramolecular network for **2** formed by hydrogen bonds and $\pi\cdots\pi$ interactions.

Table 4. Hydrogen bonds for **2**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
O1–H1A···N5^{i}	0.85	2.08	2.920(5)	170
O1–H1D···N6^{ii}	0.85	1.98	2.823(5)	172
N2–H2···S1^{iii}	0.86	2.61	3.413(4)	163
C8–H8A···O1^{iv}	0.97	2.57	3.413(6)	146

Symmetry code: ^{i}: $-x, 1-y, -z$; ^{ii}: $1+x, y, z$; ^{iii}: $x, 1+y, z$; ^{iv}: x, y, z.

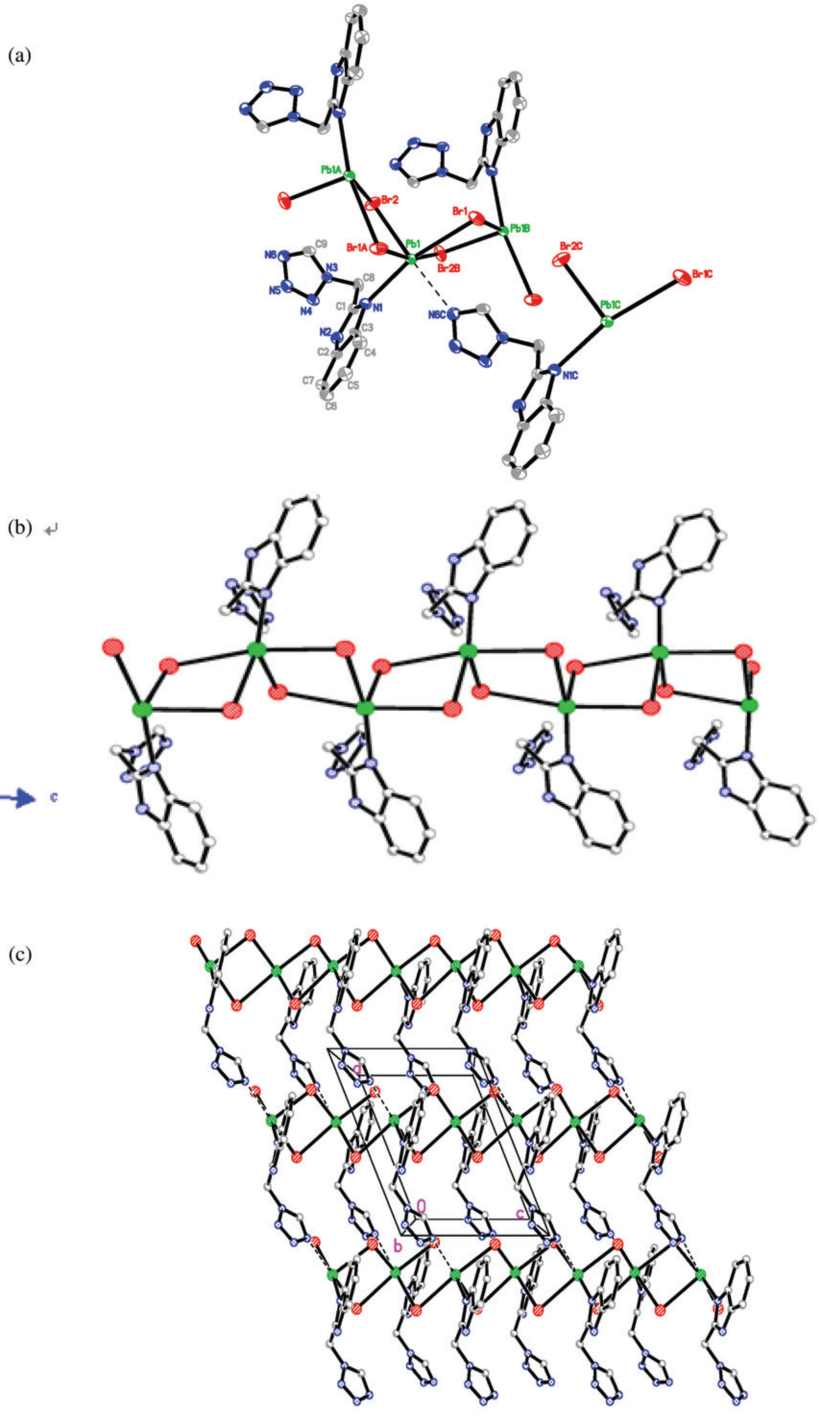


Figure 3. (a) The coordination environment of Pb(II), showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. (b) View of the 1-D chain structure of **3** along the *c*-axis. (c) View of the 2-D layer of **3** *via* Pb···N6# weak interactions. Symmetry transformations used to generate equivalent atoms: A: *x*, 1/2−*y*, 1/2+*z*; B: *x*, 1/2−*y*, −1/2+*z*; C: 1+*x*, *y*, *z*.

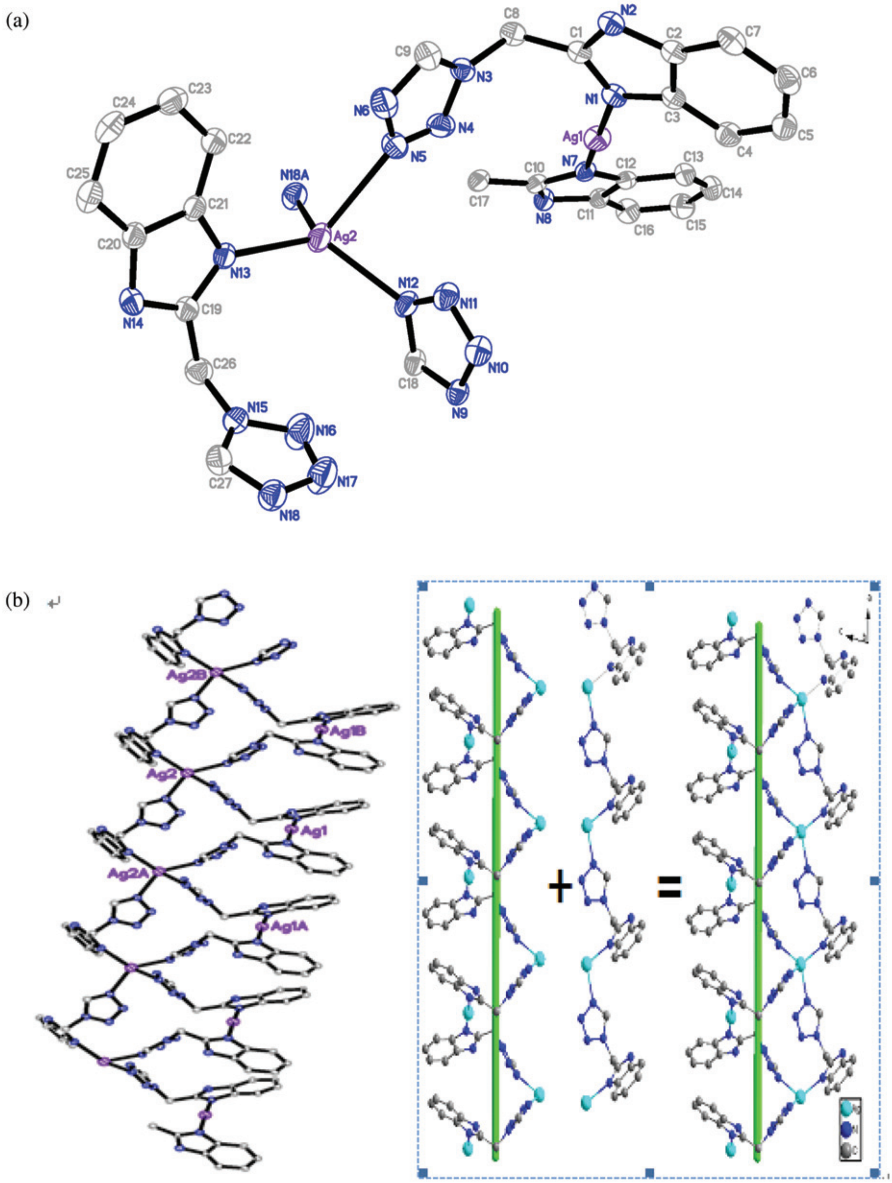


Figure 4. (a) Coordination environment of Ag(I), showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. (b) View of the 1-D helix of **4** along the *a*-axis. Symmetry transformations used to generate equivalent atoms: A: $x-1$, y, z; B: $x+1$, y, z.

tetrazole rings coordinates to Ag of different symmetry codes in the bidentate bridging mode (scheme 2, mode II). The other kind of Hbimtz coordinates to Ag of the same symmetry code in bidentate bridging mode with 1-N and 5-N (scheme 2, mode IV), in which the dihedral angle between benzimidazole and tetrazole rings is 66.5°. Each pair of linear Ag1 and tetrahedral Ag2's are bridged alternately by Hbimtz of modes IV and

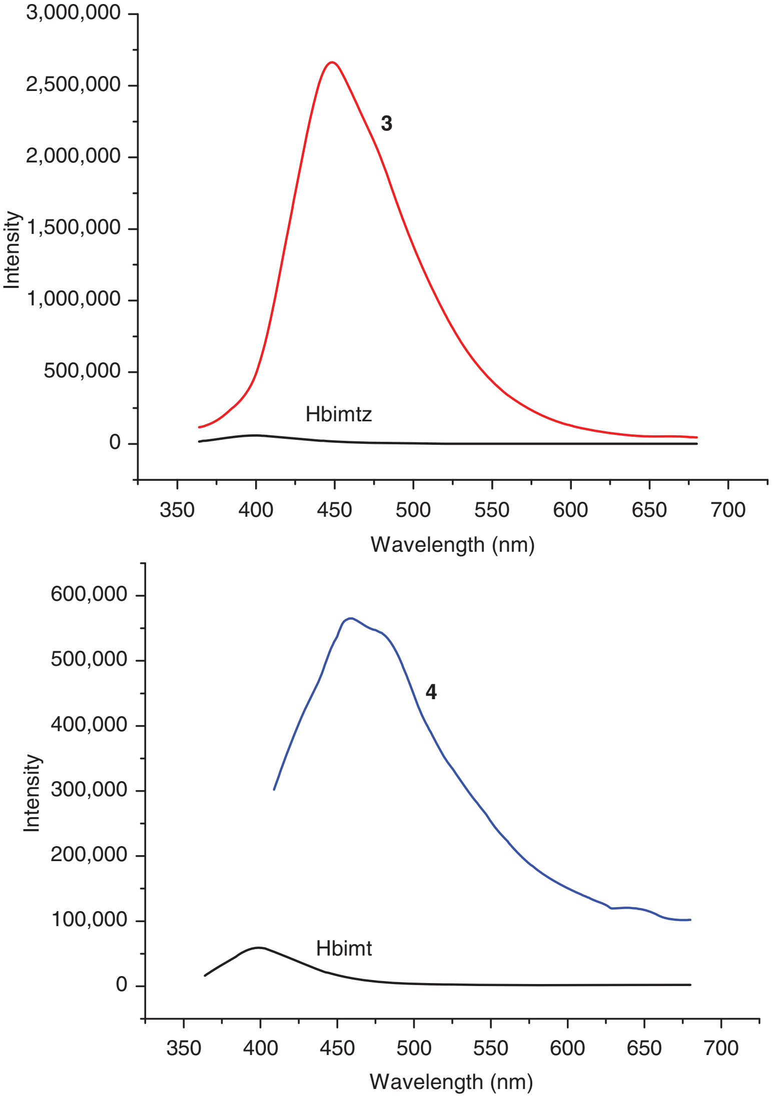


Figure 5. Emission spectra of free Hbimtz, **3**, and **4** in the solid state at room temperature.

II, and adjacent Ag2's are linked by mode I Hbimtz, forming an infinite 1-D helix chain structure along the *a*-axis (figure 4b).

3.5. *Fluorescence properties*

Solid-state fluorescence of Hbimtz, **3**, and **4** were investigated at room temperature. As shown in figure 5, Hbimtz has an intense emission at 401 nm when excited at 349 nm. Complex **3** gives emission at 447 nm upon excitation at 349 nm and **4** gives emission at 455 nm upon excitation at 395 nm. Complexes **3** and **4** display a red shift and strengthened fluorescence intensity compared to the free ligand on emission band, according to the literature [24–26], which can be ascribed to the π^*–π transfer of L, but may also contain some ligand-to-metal charge-transfer transition [27].

4. Conclusion

Four transition complexes constructed with 1-[(1H-benzimidazole-2-yl)methyl]-1,2,3,4-tetrazole have been synthesized and characterized by X-ray diffraction. Hbimtz in these complexes has different coordination modes and **1**–**4** display different topologies. Complex **1** is isomorphous with **2**. There are strong interlayer π–π stacking interactions and strong hydrogen bonds in **1** and **2**, further stabilizing the whole 3-D supramolecular network. Complex **3** was assembled to 2-D structure by μ_2-Br^- and weak bonds between Pb(II) ions and the bridging Hbimtz's. In **4**, there are two independent geometries of Ag(II) with two and four coordination. Hbimtz's bridge the two Ag(II) in different tropisms into 1-D helical chains. Photoluminescent emissions show that **3** and **4** are candidates for optical materials.

Supplementary material

CCDC Nos 801358, 801360, 801361, and 801363 contain the supplementary crystallographic data of **3**, **2**, **1** and **4**, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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