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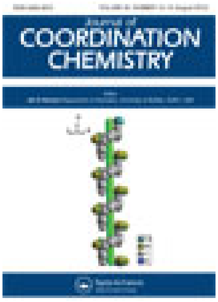

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Coordination architectures and luminescent properties of 5-(pyrimidyl)tetrazolate (Hpmtz) with group 2 metal ions

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Coordination architectures and luminescent properties of 5-(pyrimidyl)tetrazolate (Hpmtz) with group 2 metal ions

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Four alkaline earth metal-organic frameworks, $[Mg(H_2O)_6]\cdot(pmtz)_2$ (**1**), $[Ca(pmtz)_2(H_2O)_3]\cdot H_2O$ (**2**), $[Sr(pmtz)_2(H_2O)_4]$ (**3**), and $[Ba(pmtz)_2(H_2O)_2]\cdot 4H_2O$ (**4**) [pmtz = 5-(pyrimidyl)tetrazole anion], were synthesized and characterized by elemental analysis, IR spectroscopy, and X-ray crystallography. The crystal structures reveal that **1**–**3** are mononuclear while **4** displays a 2-D layer structure by bis(bidentate) bridging $pmtz^-$. The luminescence properties of **1**–**4** were investigated in the solid state at room temperature.

Keywords: Crystal structure; Alkaline earth metal; Hpmtz; Luminescence

1. Introduction

Crystal engineering techniques have been widely used for the design and synthesis of coordination frameworks with specific solid-state properties, such as electrical conductivity, molecular magnetism, molecular absorption, catalysis, ion-exchange, etc. Those techniques exploit the information encoded in the metal ion and organic ligands to direct the self-assembly of these building blocks. The building blocks dictate the crystal structures and physico-chemical properties of the resulting self-assembly product. However, it remains a challenge to design coordination compounds with the desired topologies and properties, because molecular architectures of coordination compounds are affected by organic ligands, metal ions, metal–ligand ratio, solvents, counterions, pH, and temperature [1]. Intrinsic geometric preferences of metal centers and various coordination sites of bridging ligands are the pivotal factors in determining supramolecular architectures [2].

5-Substituted 1*H*-tetrazoles are good ligands for the formation of multidimensional coordination compounds with structural diversity [3–6], a consequence of their rich coordination chemistry [7], and interesting optical [3, 4], magnetic [5], and hydrogen storage [6] properties. Among numerous tetrazole-based ligands, 5-(pyrimidyl)tetrazole

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(Hpmtz) has been studied, and a number of metal-organic coordination compounds have been prepared [8]. Thanks to the high number of nitrogen donors on the pyrimidyl and tetrazolate rings, it could exhibit a variety of coordination modes. It can act as a chelating ligand (through the tetrazolate-N1, pyrimidyl-N) similar to 2,2-bipyridine. In a non-chelating mode, $pmtz^-$ can also coordinate metallic centers through the tetrazolate-N2 and N3 nitrogens, mimicking the most common *N,N*-exobidentate mode of pyrazolates [7]. Accordingly, $pmtz^-$ is an ideal candidate for obtaining varied metal-organic frameworks. In spite of this, as far as we know, no examples of coordination compounds assembled by alkaline earth metal salts with Hpmtz have been reported. Herein we report the synthesis, crystal structures, and luminescent properties of four alkaline earth metal coordination compounds of $pmtz^-$, $[Mg(H_2O)_6]\cdot(pmtz)_2$ (**1**), $[Ca(pmtz)_2(H_2O)_3]\cdot H_2O$ (**2**), $[Sr(pmtz)_2(H_2O)_4]$ (**3**), and $[Ba(pmtz)_2(H_2O)_2]\cdot 4H_2O$ (**4**).

2. Experimental

2.1. *Materials and methods*

All chemicals and reagents were obtained from commercial sources and used as received. Hpmtz was prepared according to the method proposed by Sharpless and Demko [9]. Elemental analyses for C, H, and N were performed with an EA1110-CHNS elemental analyzer. Photoluminescence spectra were performed on a Perkin Elmer LS55 spectrofluorometer. The FT-IR spectra were recorded on a NICOLET 380 spectrometer using pressed KBr pellets.

2.2. *Synthesis*

2.2.1. Synthesis of $[Mg(H_2O)_6]\cdot(pmtz)_2$ (1). A mixture of Hpmtz (0.0148 g, 0.1 mmol) and $MgCl_2\cdot 6H_2O$ (0.0102 g, 0.05 mmol) in a 4 : 1 ethanol : water solution (5 mL) was adjusted to pH 8.0 with KOH, heated at 80°C for 8 h with stirring, then cooled to room temperature and filtered. Slow evaporation of the filtrate in air gave colorless block single-crystals suitable for X-ray diffraction in 53% yield (based on Mg). Anal. Calcd for $C_{10}H_{18}MgN_{12}O_6$ (%): C, 28.15; H, 4.25; N, 39.40. Found (%): C, 28.33; H, 4.33; N, 39.28. (KBr pellet) (cm^{-1}): 3292 (s), 1675 (s), 1574 (s), 1525 (m), 1441 (m), 1395 (s), 1262 (m), 1170 (m), 1100 (m), 1044 (m).

2.2.2. Synthesis of $[Ca(pmtz)_2(H_2O)_3]\cdot H_2O$ (2). Compound **2** was prepared in a similar manner to **1**, except that $CaCl_2\cdot 6H_2O$ (0.0110 g, 0.05 mmol) was used instead of $MgCl_2\cdot 6H_2O$. Yield: 55% based on Ca. Anal. Calcd for $C_{10}H_{14}CaN_{12}O_4$ (%): C, 29.56; H, 3.47; N, 41.36. Found (%): C, 29.71; H, 3.50; N, 41.54. (KBr pellet) (cm^{-1}): 3288 (s), 1578 (s), 1532 (s), 1422 (m), 1396 (m), 1381 (s), 1212 (m), 1088 (m), 1014 (m), 842 (m), 740 (m), 650 (m).

2.2.3. Synthesis of $[Sr(pmtz)_2(H_2O)_4]$ (3). Compound **3** was prepared in a similar manner to **1**, except that $SrCl_2\cdot 6H_2O$ (0.0133 g, 0.05 mmol) was used instead of

$MgCl_2 \cdot 6H_2O$. Yield: 61% based on Sr. Anal. Calcd for $C_{10}H_{14}SrN_{12}O_4$ (%): C, 26.46; H, 3.11; N, 37.03. Found (%): C, 26.29; H, 3.17; N, 37.30. (KBr pellet) (cm^{-1}): 3414 (s), 1647 (s), 1571 (s), 1533 (m), 1448 (m), 1397 (s), 1232 (m), 1168 (m), 1048 (m), 825 (m), 739 (m), 641 (m).

2.2.4. Synthesis of $[Ba(pmtz)_2(H_2O)_2] \cdot 4H_2O$ (4). Compound **4** was prepared in a similar manner to **1**, except that $BaCl_2 \cdot 6H_2O$ (0.0158 g, 0.05 mmol) was used instead of $MgCl_2 \cdot 6H_2O$. Yield: 65% based on Ba. Anal. Calcd for $C_{10}H_{18}BaN_{12}O_6$ (%): C, 22.26; H, 3.36; N, 31.15. Found (%): C, 22.39; H, 3.28; N, 31.34. (KBr pellet) (cm^{-1}): 3410 (s), 1655 (s), 1572 (s), 1522 (m), 1419 (m), 1393 (s), 1258 (m), 1163 (m), 1042 (m), 814 (m), 738 (m), 642 (m).

2.3. *X-ray crystallography*

Suitable single crystals of **1–4** were mounted on a Rigaku SCXmini-CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 291 K. The intensity data were collected by the ω scan technique and reduced using the Crystal Clear program [10]. The crystal structures of **1–4** were solved by direct methods and refined on F^2 by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms [11]. Hydrogen atoms were generated geometrically and refined using a riding model. Crystallographic data and other pertinent information for **1–4** are summarized in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Preparation and characterization of 1–4*

Compounds **1–4** were obtained as colorless crystals by the treatment of Hpmtz with MCl_2 [M(II) = Mg, Ca, Sr, Ba] through evaporation method at room temperature in aqueous and ethanol solution at pH = 8.0 adjusted with KOH in the molar ratio Hpmtz/M(II) 2 : 1. They were relatively stable toward oxygen and moisture. The elemental analyses of **1–4** were consistent with their chemical formulas. IR spectra of the products showed peaks (1393–1675 cm^{-1}) of the tetrazolate and pyrimidyl groups in $pmtz^-$ [7]. The identities of **1–4** were finally confirmed by X-ray crystallography.

3.2. *Description of crystal structures of 1–4*

3.2.1. $[Mg(H_2O)_6] \cdot (pmtz)_2$ (1). Complex **1** consists of neutral mononuclear structure, crystallizing in the monoclinic space group *C2/c* and the asymmetric unit containing one-half of $[Mg(H_2O)_6]^{2+}$ and one $pmtz^-$. As shown in figure 1, the Mg(II) located on an inversion center is coordinated by six water molecules forming a slightly distorted octahedron. The Mg–O bond lengths [2.0393(18)–2.124(2) Å] (table 2) for **1** are in agreement with the literature values for Mg–O(W) complexes [12]. The dihedral

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

Compound	**1**	**2**	**3**	**4**
Molecular formula	$C_{10}H_{18}MgN_{12}O_6$	$C_{10}H_{14}CaN_{12}O_4$	$C_{10}H_{14}SrN_{12}O_4$	$C_{10}H_{18}BaN_{12}O_6$
Formula weight	426.67	406.41	453.95	539.70
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$	$Pbcn$
Unit cell dimensions (Å, °)				
a	9.4374(19)	7.9348(16)	8.3298(17)	10.297(2)
b	13.734(3)	16.232(3)	16.230(3)	11.245(2)
c	14.828(3)	12.730(3)	12.735(3)	17.882(4)
β	104.73(3)	90.84(3)	95.24(3)	90.00
Volume (Å^3), Z	1858.8(6), 4	1639.4(6), 4	1714.5(6), 4	2070.6(7), 4
Temperature (K)	291(2)	291(2)	291(2)	291(2)
Calculated density (g cm^{-3})	1.525	1.647	1.759	1.731
Absorption coefficient (mm^{-1})	0.155	0.434	3.194	1.972
Independent reflection	2130 [R(int) = 0.0512]	3765 [R(int) = 0.0600]	3930 [R(int) = 0.0983]	2322 [R(int) = 0.0644]
Reflections collected	1467	2894	2686	1651
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0613$, $wR_2{}^b = 0.1640$	$R_1{}^a = 0.0594$, $wR_2{}^b = 0.1605$	$R_1{}^a = 0.0489$, $wR_2{}^b = 0.1124$	$R_1{}^a = 0.0383$, $wR_2{}^b = 0.1230$
Goodness-of-fit on $F^{2\,c}$	1.168	1.026	0.759	0.971
Max. and min. transmission	0.663 and −0.525	0.321 and −0.441	0.388 and −0.391	0.499 and −0.839

[a] $R_1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$.

[b] $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

[c] Goodness-of-fit on $F^2 = \{\Sigma[w((F_o^2 - F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.

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

Complex **1**					
Mg(1)–O(1)	2.0393(18)	Mg(1)–O(2)	2.124(2)	Mg(1)–O(3)	2.0599(18)
O(1)–Mg(1)–O(3)	90.82(8)	O(1A)–Mg(1)–O(3)	89.18(8)	O(1)–Mg(1)–O(2)	89.37(8)
O(1A)–Mg(1)–O(2)	90.63(8)	O(3)–Mg(1)–O(2)	89.33(8)		
Complex **2**					
Ca(1)–O(1)	2.3618	Ca(1)–O(2)	2.3175	Ca(1)–O(3)	2.320(2)
Ca(1)–N(1)	2.502(2)	Ca(1)–N(7)	2.513(2)	Ca(1)–N(5)	2.621(2)
Ca(1)–N(11)	2.624(2)	Ca(1)–O(4)	4.012		
O(2)–Ca(1)–O(3)	94.05(6)	O(2)–Ca(1)–O(1)	175.4	O(3)–Ca(1)–O(1)	90.52(6)
O(2)–Ca(1)–N(1)	79.08(6)	O(3)–Ca(1)–N(1)	84.51(8)	O(1)–Ca(1)–N(1)	101.46(6)
O(2)–Ca(1)–N(7)	80.61(6)	O(3)–Ca(1)–N(7)	137.60(8)	O(1)–Ca(1)–N(7)	95.96(6)
N(1)–Ca(1)–N(7)	134.25(8)	O(2)–Ca(1)–N(5)	99.72(5)	O(3)–Ca(1)–N(5)	142.76(8)
O(1)–Ca(1)–N(5)	76.57(5)	N(1)–Ca(1)–N(5)	64.71(7)	N(7)–Ca(1)–N(5)	79.08(8)
O(2)–Ca(1)–N(11)	103.12(6)	O(3)–Ca(1)–N(11)	75.92(8)	O(1)–Ca(1)–N(11)	77.93(6)
N(1)–Ca(1)–N(11)	160.40(8)	N(7)–Ca(1)–N(11)	64.74(7)	N(5)–Ca(1)–N(11)	132.67(7)
Complex **3**					
Sr(1)–O(1)	2.549(3)	Sr(1)–O(2)	2.608(3)	Sr(1)–O(3)	2.691(3)
Sr(1)–O(4)	2.509(3)	Sr(1)–N(1)	2.732(4)	Sr(1)–N(7)	2.765(4)
Sr(1)–N(5)	2.831(4)	Sr(1)–N(11)	2.867(4)		
O(4)–Sr(1)–O(1)	104.18(11)	O(4)–Sr(1)–O(2)	84.51(11)	O(1)–Sr(1)–O(2)	168.27(10)
O(4)–Sr(1)–O(3)	66.21(10)	O(1)–Sr(1)–O(3)	71.15(10)	O(2)–Sr(1)–O(3)	120.13(10)
O(4)–Sr(1)–N(1)	107.74(11)	O(1)–Sr(1)–N(1)	113.40(11)	O(2)–Sr(1)–N(1)	70.30(11)
O(3)–Sr(1)–N(1)	71.08(11)	O(4)–Sr(1)–N(7)	118.66(11)	O(1)–Sr(1)–N(7)	92.42(11)
O(2)–Sr(1)–N(7)	76.35(10)	O(3)–Sr(1)–N(7)	163.52(11)	N(1)–Sr(1)–N(7)	118.64(11)
O(4)–Sr(1)–N(5)	167.31(10)	O(1)–Sr(1)–N(5)	79.71(10)	O(2)–Sr(1)–N(5)	93.50(10)
O(3)–Sr(1)–N(5)	104.54(10)	N(1)–Sr(1)–N(5)	60.00(10)	N(7)–Sr(1)–N(5)	72.75(11)
O(4)–Sr(1)–N(11)	70.76(10)	O(1)–Sr(1)–N(11)	72.30(11)	O(2)–Sr(1)–N(11)	103.95(11)
O(3)–Sr(1)–N(11)	112.57(10)	N(1)–Sr(1)–N(11)	174.24(11)	N(7)–Sr(1)–N(11)	59.02(10)
N(5)–Sr(1)–N(11)	121.79(10)				
Complex **4**					
Ba(1)–O(1)	2.846(2)	Ba(1)–N(1)	2.969(4)	Ba(1)–N(4B)	3.013(4)
Ba(1)–N(6B)	3.0781(19)	Ba(1)–N(5A)	3.089(4)		
O(1)–Ba(1)–O(1A)	172.28(7)	O(1A)–Ba(1)–N(1)	75.80(9)	O(1A)–Ba(1)–N(1A)	108.41(9)
O(1A)–Ba(1)–N(4B)	68.19(9)	N(1A)–Ba(1)–N(4B)	154.67(11)	O(1)–Ba(1)–N(4C)	68.19(9)
N(4B)–Ba(1)–N(4C)	70.32(18)	O(1A)–Ba(1)–N(6A)	111.83(6)		

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

plane between the pyrimidyl and the tetrazolate ring is twisted by 21.7°. None of the nitrogen atoms coordinate, but act as acceptors of O–H $\cdots$ N hydrogen bonds. Two coordinated water molecules (O3, O3A) connect $[Mg(H_2O)_6]^{2+}$ two $pmtz^-$ through O(3) $\cdots$ N(3) and O(3A) $\cdots$ N(3A) intramolecular hydrogen bonds. Each mononuclear unit $[Mg(H_2O)_6] \cdot (pmtz)_2]^+$ is bridged through four kinds of hydrogen bonds [O–H $\cdots$ N] (table 3) to form a 2-D supramolecular network structure extended along the *ac* plane (figure 2).

3.2.2. $[Ca(pmtz)_2(H_2O)_3] \cdot H_2O$ (2). Species **2** crystallizes in the monoclinic space group *P21/n* and the asymmetric unit contains one $[Ca(pmtz)_2(H_2O)_3] \cdot H_2O$. A drawing of the structural motif is shown in figure 3. Each calcium is seven-coordinate by four nitrogen atoms from two bidentate chelating $pmtz^-$ and three water molecules, forming a slightly distorted pentagonal bipyramid with two of the water molecules in axial positions (O1 and O2); the other water molecule and the four N atoms of the two $pmtz^-$

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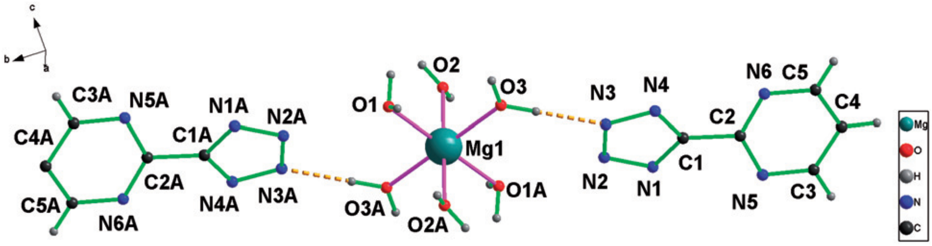

Figure 1. The coordination environment of Mg(II) of **1**. A: ½ − x, 3/2 − y, 1 − z.

Table 3. Hydrogen-bonding geometry (Å and °) for **1**–**4**.

D–H···A	D–H	H···A	D···A	∠D–H···A
Complex **1**				
O(3)–H(3C)···N(3)	0.85	2.03	2.870(3)	172
O(2)–H(2A)···N(5)$^{\#1}$	0.85	2.20	3.027(3)	165
O(2)–H(2B)···N(1)$^{\#2}$	0.85	2.15	3.001(3)	175
O(3)–H(3B)···N(4)$^{\#3}$	0.85	2.00	2.816(4)	160
Complex **2**				
O(1)–H(1A)···N(10)$^{\#4}$	0.96	1.85	2.7971	166
O(1)–H(1B)···N(4)$^{\#5}$	0.92	1.98	2.8858	168
O(2)–H(2A)···N(12)$^{\#6}$	0.85	2.05	2.8755	164
O(2)–H(2B)···N(6)$^{\#7}$	0.85	2.01	2.8240	160
O(3)–H(3B)···O(4)	0.86	1.92	2.6761	172
O(3)–H(3C)···N(2)$^{\#8}$	0.81	2.17	2.968	169
O(4)–H(4B)···N(9)$^{\#4}$	0.85	2.01	2.8481	168
O(4)–H(4C)···O(1)$^{\#9}$	0.85	2.18	3.0071	164
Complex **3**				
O(1)–H(1B)···N(10)$^{\#10}$	0.85	2.00	2.835(5)	169
O(1)–H(1A)···N(4)$^{\#11}$	0.85	2.01	2.856(5)	171
O(2)–H(2B)···N(12)$^{\#12}$	0.85	2.19	3.010(5)	163
O(2)–H(2A)···N(6)$^{\#13}$	0.85	2.04	2.878(5)	167
O(3)–H(3D)···N(9)$^{\#11}$	0.85	2.16	2.877(5)	141
O(4)–H(4B)···N(2)$^{\#14}$	0.85	1.99	2.775(5)	154
O(4)–H(4C)···O(2)$^{\#14}$	0.85	2.10	2.924(4)	163
O(3)–H(3C)···O(1)$^{\#15}$	0.85	2.41	3.222(5)	161
Complex **4**				
O(2)–H(2A)···N(2)	0.96	2.01	2.8365	144
O(3)–H(3B)···O(1)$^{\#16}$	0.96	2.14	2.9366	139
O(1)–H(1A)···O(2)^{17}	0.96	2.16	2.8540	128

Symmetry codes for **1**: (#1) x, $1-y$, $-1/2+z$; (#2) $-x$, $1-y$, $1-z$; (#3) $1-x$, $1-y$, $1-z$; for **2**: (#4) $1/2+x$, $1/2-y$, $1/2+z$; (#5) $1/2+x$, $1/2-y$, $-1/2+z$; (#6) $-1/2+x$, $1/2-y$, $1/2+z$; (#7) $-1/2+x$, $1/2-y$, $-1/2+z$; (#8) $-x$, $-y$, $1-z$; (#9) $1-x$, $-y$, $1-z$; for **3**: (#10) $1/2+x$, $1/2-y$, $-1/2+z$; (#11) $1/2+x$, $1/2-y$, $1/2+z$; (#12) $-1/2+x$, ½ − y, $-1/2+z$; (#13) $-1/2+x$, $1/2-y$, $1/2+z$; (#14) $1-x$, $-y$, $2-z$; (#15) $2-x$, $-y$, $2-z$; for **4**: (#16) x, $1-y$, $1/2+z$; (#17) x, $-y$, $-1/2+z$.

ligands occupy approximately the five positions around the almost planar equator. The interatomic Ca–pryamidyl N bond distances [2.621(2), 2.624(2) Å] are slightly longer than Ca–tetrazole N bond distances [2.502(2), 2.513(2) Å], which can be compared to the corresponding values in the literature (Ca–N = 2.311–2.583(3) Å) [13]. Each pmtz$^-$ chelates to Ca(II) through one tetrazolate nitrogen and one pyrimidyl nitrogen. The dihedral planes of the pyrimidyl and the tetrazolate rings of two pmtz$^-$

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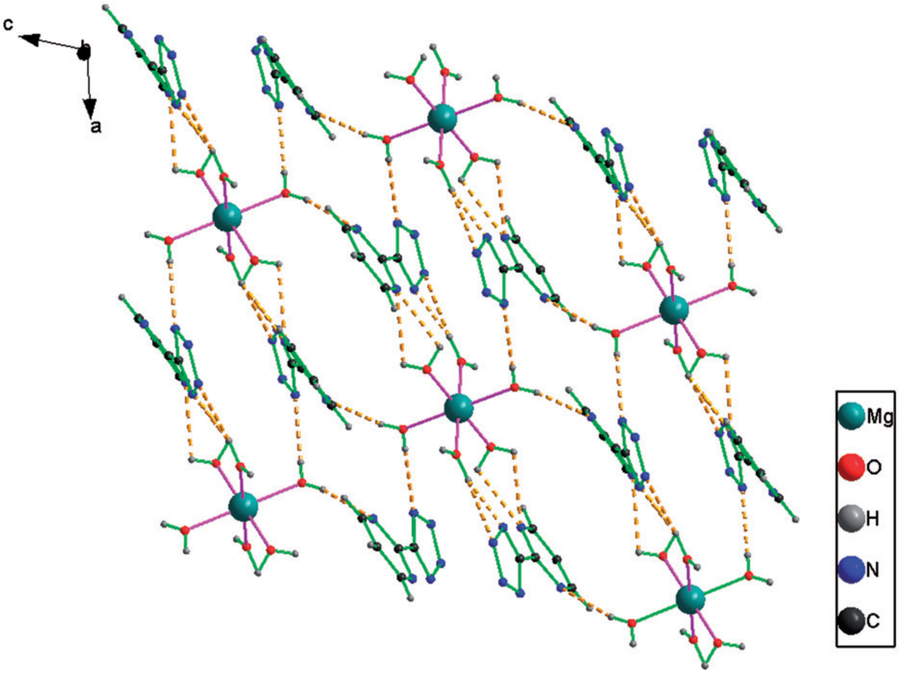

Figure 2. The 2-D network structure of **1** formed *via* H-bonding interactions.

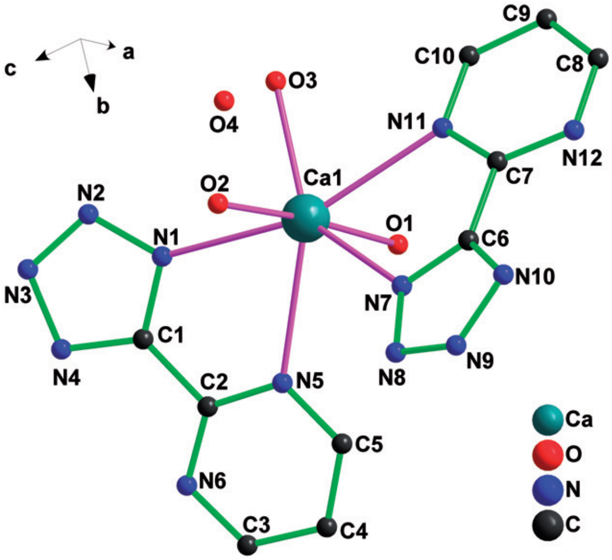

Figure 3. The coordination environment of Ca(II) of **2**.

are twisted by 13.9° and 8.6°, respectively. In the crystal structure of **2**, eight intermolecular O···N(O) hydrogen bonds (details of which are given in table 3) link each Ca(II) complex to form a 3-D supramolecular network structure, as illustrated in figure 4.

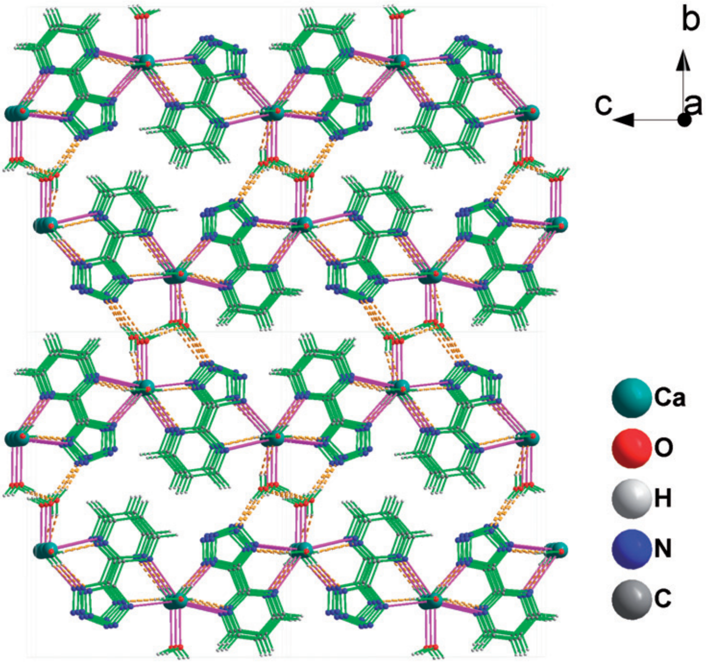

Figure 4. The 3-D network structure of **2** formed *via* H-bonding interactions.

3.2.3. [Sr(pmtz)$_2$(H$_2$O)$_4$] (3). Complex **3** crystallizes in the monoclinic space group $P2_1/n$ with the asymmetric unit consisting of two pmtz$^-$, one strontium, and four water molecules. X-ray crystallography shows that **3** is mononuclear (figure 5). Each strontium is eight-coordinate with four nitrogen atoms from two chelating pmtz$^-$ and four water molecules, forming a distorted square-antiprism. Each pmtz$^-$ chelates to Sr(II) through one tetrazolate nitrogen and one pyrimidyl nitrogen. The dihedral planes of the pyrimidyl and tetrazolate rings of two pmtz$^-$ are twisted by 13.8° and 4.5°, respectively. The Sr–O bond lengths [2.509(3)–2.691(3) Å] and Sr–N bond lengths [2.732(4)–2.867(4) Å] are typical for Sr–O(N) [12b, 13]. The essential difference between **3** and **2** is the Ca1–O4 bond distance of 4.012 Å, which is significantly longer than the Sr1–O4 bond distance of 2.509(3) Å. In the crystal structure of **3**, eight intermolecular O $\cdots$ N(O) hydrogen bonds (details of which are given in table 3) link each Sr(II) complex to form a 3-D supramolecular network structure, as illustrated in figure 6. Each O–H group of coordinated water molecule is a hydrogen bond donor, and uncoordinated tetrazolate nitrogen atoms (N2, N4, N9, N10) and the pyrimidyl nitrogen atoms (N6, N12) and oxygen atoms (O1, O2) of the coordinated water molecule are hydrogen bond acceptors.

3.2.4. [Ba(pmtz)$_2$(H$_2$O)$_2$] · 4H$_2$O (4). X-ray structure analysis reveals that **4** crystallizes in orthorhombic space group *Pbcn* and the asymmetric unit contains one-half of [Ba(pmtz)$_2$(H$_2$O)$_2$] · 4H$_2$O. In the structure, each barium located on an inversion center is 10-coordinate (N$_8$O$_2$) to form a distorted bicapped square-antiprism geometry

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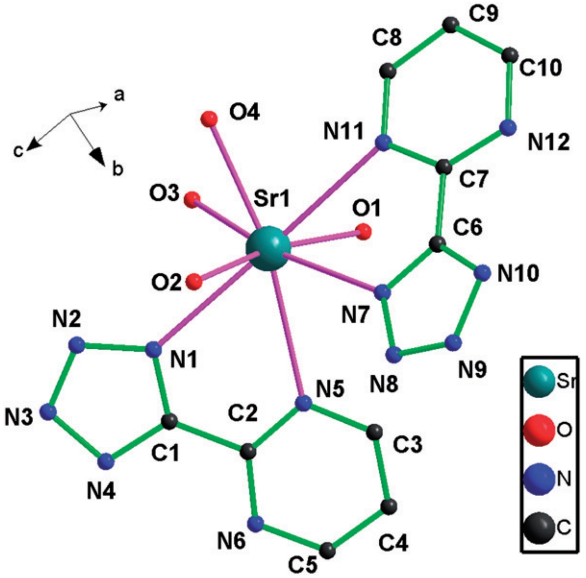

Figure 5. The coordination environment of Sr(II) of **3**.

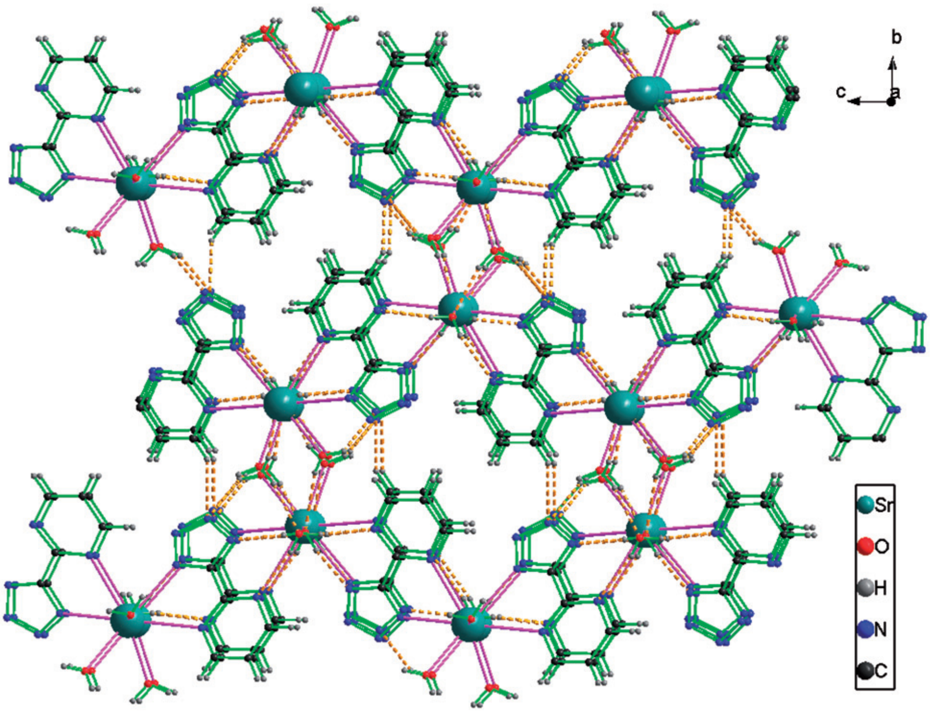

Figure 6. The 3-D network structure of **3** formed *via* H-bonding interactions.

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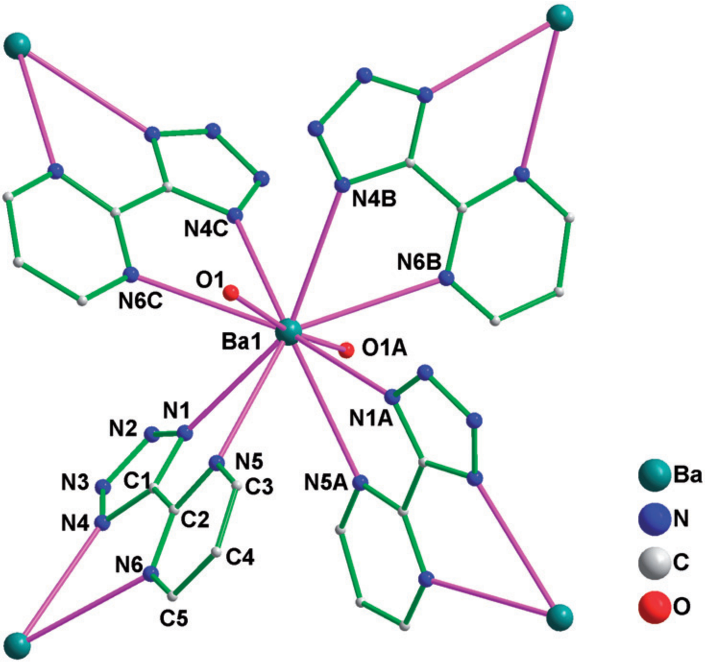

Figure 7. The coordination environment of Ba(II) of **4**.

with the eight nitrogen atoms belonging to four bis(bidentate) pmtz$^-$ ligands and two water molecules (figure 7). The distances of Ba–N [2.969(4)–3.089(4) Å], slightly longer than Ba–O [2.846(2) Å] are typical values for Ba–N(O) coordination distances [12, 13]. Each ligand is coordinated to Ba^{2+} through the tetrazole nitrogen (N_1 or N_4) and pyrimidyl nitrogen (N_5 or N_6) in bis(bidentate) coordination, giving four stable five-membered chelate rings (C_2N_2Ba) around the Ba(II) center and generating 2-D square-grid-like sheets parallel to the *ab* plane (figure 8), with a Ba$\cdots$Ba distance of 7.624 Å and the Ba$\cdots$Ba$\cdots$Ba bite angle of 180.00° or 95.04°. Therefore, **4** is an example of 5-substituted-tetrazolate bridged complexes containing the μ_4-k^2N1, N5: k^2 N4, N6 coordination. The equivalent torsion angle is 13.7° in pmtz$^-$. In the crystal structure of **4**, adjacent 2-D layers in a face-to-face manner are further packed into a 3-D supramolecular architecture by three O$\cdots$N(O) hydrogen bonds (table 3; figure 9).

3.3. *Luminescence properties of 1–4 and free ligand*

Metal-organic compounds have been reported to affect the emission wavelength and intensity of organic materials through metal coordination [14]. Photoluminescent behaviors of **1**–**4** and free Hpmtz are studied in the solid state at room temperature. Emission spectra of **1**–**4** and Hpmtz are depicted in figure 10. Excitation at 369 nm leads to fluorescence with an emission maximum at 450 nm for free Hpmtz; compounds **1**–**4** (when excited at 334, 313, 328, and 325 nm, respectively) present one intense (and broad) emission at 396, 367, 393, and 391 nm, respectively. The emissions may be

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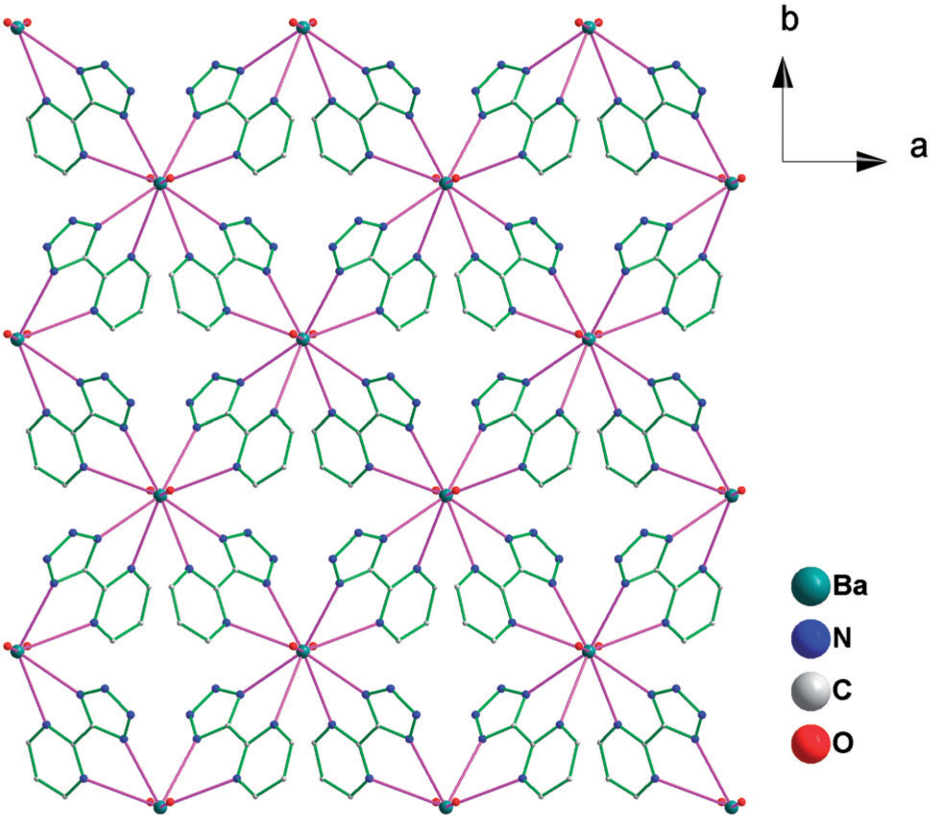

Figure 8. 2-D coordination network of **4** extended along the *ab* plane (hydrogen atoms are omitted for clarity).

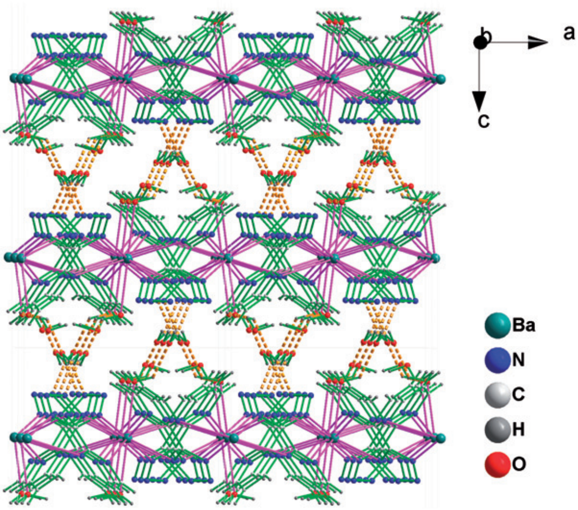

Figure 9. The 3-D network structure of **4** formed *via* H-bonding interactions.

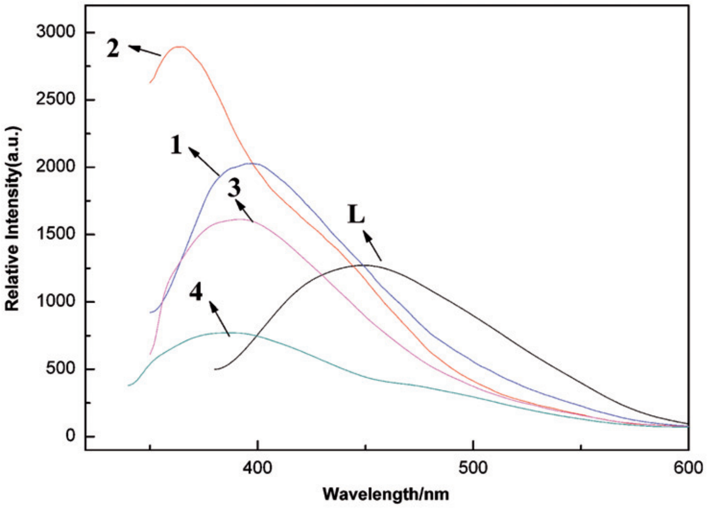

Figure 10. Solid-state fluorescence spectra for Hpmtz and **1–4**.

assigned to an intra-ligand transfer because similar emissions are at 450 nm for the free ligand. Compared with the emission spectrum of Hpmtz, the relative intensity of emission spectra of **1**–**3** are stronger, whereas **4** is lower; a concomitant blue shift of about 54–83 nm in **1**–**4** is observed. The blue shift of emission peak and luminescent densities occur in **1**–**4** to different degrees, attributed to the heavy-atom effect, structural diversification depending on the metal ions and preparing conditions [14, 15].

4. Summary

Under the same experimental conditions, reaction of Hpmtz with alkaline earth metal salts MCl_2 [M(II) = Mg, Ca, Sr, Ba] gives four group 2 metal-organic complexes with different structures. The coordination number increases from 6 (magnesium), 7 (calcium) to 8 (strontium), and finally to 10 (barium) as a result of increase in ionic radii. Complexes **1**–**3** consist of neutral mononuclear structures and **4** generates a 2-D layer network by bis(bidentate) bridging $pmtz^-$.

Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-809451 (**1**), CCDC-809450 (**2**), 809452 (**3**), and 809449 (**4**). Copies of the data can be obtained free of charge on application to CHGC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or Email: deposit@ccdc.cam.ac.uk).

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