



Three new alkaline earth coordination compounds based on 5-(2-pyrimidyl)tetrazole-2-acetic acid



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ABSTRACT

Reactions of Hpymtza (Hpymtza = 5-(2-pyrimidyl)tetrazole-2-acetic acid) with MCl_2 ($M = Mg(II), Sr(II), Ba(II)$), produced three new coordination compounds, $[Mg(H_2O)_6] \cdot 2pymtza \cdot H_2O$ (**1**), $[Sr(pymtza)_2(H_2O)_2] \cdot 4H_2O$ (**2**), $[Ba(pymtza)_2(H_2O)_4] \cdot H_2O$ (**3**). These compounds were characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. Compound **1** shows a mononuclear structure while **2** and **3** reveal 1-D structures via bridging pymtza as linker. Furthermore, the luminescent properties of **1–3** were investigated at room temperature in the solid state.

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1. Introduction

From the view point of crystal engineering, the shapes of the organic ligands are very important in forming the final structures of the coordination frameworks. One of the important characteristics of an organic compound used as a ligand is its diverse coordination modes, molecular rigidity and flexibility, and to determine the orientation of the binding sites [1,2]. As versatile building clusters, carboxylate-tetrazole compounds have been employed extensively as multidentate chelating or bridging linkers because of both the carboxylate and tetrazole group being able to participate in mono-, bi-, and multidentate coordination modes with central metal ions, so they can be used as linkers to design and construct varied structural and functional coordination complexes and therefore greatly increase the chances of their potential industrial applications in the field of heterogeneous catalysis, optical properties, magnetism and luminescence. Among multitudinous tetrazole-containing carboxylate ligands, tetrazolate-5-acetic acid [3], tetrazolate-5-formic acid [4], tetrazole-1-acetic acid [5], 5-aminotetrazole-1-acetic acid [6], 5-(2-pyrazinyl)tetrazole-2-acetic acid [7], 5-(2-pyridyl)tetrazole-2-acetic acid [8], 5-[N-acetato(3-pyridyl)]tetrazole [9], 5-[N-acetato(4-pyridyl)]tetrazole [10], 5-[(4-nitryl)phenyl] tetrazole-1-acetato [11], etc., have proven to be good candidates for the construction of novel coordination compounds. However, the compounds based on

5-(2-pyrimidyl)tetrazole-2-acetic acid ligand (Hpymtza), a new tetrazole-containing carboxylate ligand (Scheme 1), have been less studied, to the best of our knowledge. The Hpymtza ligand simultaneously comprises N atoms of pyrimidine and tetrazole rings and O atoms of carboxylate which should display more flexible coordination fashions, and the $-CH_2-$ spacer between the tetrazole ring and carboxylate group offers flexible orientations of the carboxylate arm, allowing the formation of varied framework structures. In this paper, we describe the synthesis, crystal structures and luminescent properties of the three new coordination compounds $[Mg(H_2O)_6] \cdot 2pymtza \cdot H_2O$ (**1**), $[Sr(pymtza)_2(H_2O)_2] \cdot 4H_2O$ (**2**), $[Ba(pymtza)_2(H_2O)_4] \cdot H_2O$ (**3**).

2. Experimental

2.1. Materials and methods

In this study, 5-(2-pyrimidyl)tetrazole was prepared by [2 + 3] cycloaddition, by treating 2-cyanopyrimidine with NaN_3 in toluene in the presence of triethylammonium chloride. The reaction of 5-(2-pyrimidyl)tetrazole with chloroacetic acid in methanolic potassium hydroxide solution gave mostly H(tetrazole)-substituted products (Kpymtza), which was further purified by adjusting the pH to 2 with HCl, forming the corresponding acid product (Hpymtza). Other chemicals were commercially available reagents of analytical grade and used without further purification. The elemental analysis for C, H and N were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. The IR spectra were recorded ($4000-400\text{ cm}^{-1}$) on a NICOLET 380 spectrometer with pressed

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KBr pellets. The photoluminescent spectra were performed on a Hitachi F4600 spectrofluorometer.

2.2. Synthesis of $[Mg(H_2O)_6] \cdot 2pymtza \cdot H_2O$ (**1**)

A mixture of $MgCl_2 \cdot 6H_2O$ (0.0406 g, 0.2 mmol) and Hpymtza (0.0824 g, 0.4 mmol) in mixture of EtOH (6 ml) and water (2 mL) was adjusted to pH 6 with NaOH (0.5 mol/L) and sealed in a 25 mL teflon-lined stainless steel container, which was heated at 120 °C for 48 h. After the sample was cooled to room temperature, colorless block crystals **1** were obtained. For **1**, yield: 53% based on Mg. *Anal. Calc.* for $C_{14}H_{24}MgN_{12}O_{11}$: C, 29.99; H, 4.31; N, 29.98. Found: C, 30.22; H, 4.20; N, 29.61%. IR (KBr, cm^{-1}): 3431(s), 1625(s), 1570(m), 1435(m), 1385(s), 1315(m), 1199(w), 1130(w), 1083(w), 920(s), 827(w), 741(w), 645(w), 647(m), 588(w).

2.3. Synthesis of $[Sr(pymtza)_2(H_2O)_2] \cdot 4H_2O$ (**2**) and $[Ba(pymtza)_2(H_2O)_4] \cdot H_2O$ (**3**)

An identical procedure to that of **1** was followed to prepare **2** and **3**, respectively, except that $MgCl_2 \cdot 6H_2O$ was replaced by $SrCl_2 \cdot 6H_2O$ or $BaCl_2 \cdot 2H_2O$. Colorless crystals of **2** and **3** were obtained. For **2**, yield: 55% based on Sr. *Anal. Calc.* for $C_{14}H_{22}SrN_{12}O_{10}$: C, 27.75; H, 3.66; N, 27.74. Found: C, 27.91; H, 3.54; N, 27.53%. IR (KBr, cm^{-1}): 3474(s), 1610(s), 1570(m), 1391(s), 1309(m), 1247(m), 1161(w), 1130(w), 1087(w), 921(s), 824(w), 710(w), 635(w), 640(m), 585(w). For **3**, yield: 63% based on Ba. *Anal. Calc.* for $C_{14}H_{20}BaN_{12}O_9$: C, 26.37; H, 3.16; N, 26.36. Found: C, 26.18; H, 3.22; N, 26.23%. IR (KBr, cm^{-1}): 3477(s), 1607(s), 1571(m), 1382(s), 1310(m), 1190(w), 1160(w), 1130(w), 1079(w), 918(m), 819(m), 739(w), 677(w), 635(m), 589(w).

2.4. X-ray crystallography

Single crystal X-ray crystal data were collected on a Rigaku SCX mini CCD diffractometer equipped with a graphite-monochromated

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

Compound	1	2	3
Empirical formula	$C_{14}H_{24}MgN_{12}O_{11}$	$C_{14}H_{22}SrN_{12}O_{10}$	$C_{14}H_{20}BaN_{12}O_9$
Formula mass	560.76	606.06	637.75
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	<i>C2/c</i>	<i>P nma</i>	<i>P2/c</i>
<i>a</i> (Å)	22.230(4)	7.2919(15)	10.276(2)
<i>b</i> (Å)	6.8685(14)	37.309(8)	7.0256(14)
<i>c</i> (Å)	18.949(4)	9.0444(18)	18.098(6)
α (°)			
β (°)	122.00(3)		115.21(2)
γ (°)			
<i>V</i> (Å ³)	2453.6(12)	2460.6(9)	1182.1(5)
<i>Z</i>	4	4	2
<i>T</i> (K)	291(2)	291(2)	291(2)
<i>D</i> _{calcd} (g cm ⁻³)	1.518	1.636	1.792
μ (mm ⁻¹)	0.152	2.265	1.751
Reflections collected	11969	14454	10954
Unique reflections (<i>R</i> _{int})	2809 (0.0828)	2856 (0.1066)	2705 (0.0529)
No. observations (<i>I</i> > 2.00 σ (<i>I</i>))	1785	1782	2481
No. Variables	164	174	165
<i>R</i> ^a , <i>wR</i> ^b	0.0950, 0.2007	0.0578, 0.1345	0.0339, 0.1034
Goodness-of-fit (GOF) ^c	1.108	0.905	0.828
Δ/ρ_{max} (e/Å ³)	0.550	0.476	0.746
Δ/ρ_{min} (e/Å ³)	-0.440	-0.459	-0.817

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $Rw = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$.

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

Table 2
Selected bond distances (Å) and angles (°) for **1–3**.

$C_{14}H_{24}MgN_{12}O_{11}$ (1)			
Mg(1)–O(5)	2.0597	Mg(1)–O(4)	2.0870
Mg(1)–O(3)	2.1020		
O(5)–Mg(1)–O(3)	92.3	O(5)–Mg(1)–O(4A)	89.9
O(5)–Mg(1)–O(4)	90.1	O(4)–Mg(1)–O(3)	90.1
O(3)–Mg(1)–O(3A)	87.7	O(4)–Mg(1)–O(3A)	89.9
$C_{14}H_{22}SrN_{12}O_{10}$ (2)			
Sr(1)–O(1)	2.663	Sr(1)–O(1C)	2.526
Sr(1)–O(2)	2.772	Sr(1)–O(3)	2.748
Sr(1)–O(3A)	2.852	Sr(1)–O(4)	2.537
O(1)–Sr(1)–O(1B)	138.437	O(1)–Sr(1)–O(1C)	93.942
O(1)–Sr(1)–O(2)	47.770	O(1)–Sr(1)–O(2B)	113.243
O(1)–Sr(1)–O(3)	143.855	O(1)–Sr(1)–O(3A)	65.281
O(1)–Sr(1)–O(4)	87.600	O(1C)–Sr(1)–O(1D)	73.509
O(1C)–Sr(1)–O(2)	73.096	O(1C)–Sr(1)–O(2B)	146.461
O(1C)–Sr(1)–O(3)	68.615	O(1C)–Sr(1)–O(3A)	73.155
O(1C)–Sr(1)–O(4)	130.804	O(2)–Sr(1)–O(2B)	139.910
O(2)–Sr(1)–O(3)	96.164	O(2)–Sr(1)–O(3A)	99.873
O(2)–Sr(1)–O(4)	72.143	O(3)–Sr(1)–O(3A)	137.725
O(3)–Sr(1)–O(4)	81.719	O(3A)–Sr(1)–O(4)	146.555
$C_{14}H_{20}BaN_{12}O_9$ (3)			
Ba(1)–O(4)	2.793	Ba(1)–O(2B)	2.834
Ba(1)–O(3)	2.938	Ba(1)–N(1)	3.008
Ba(1)–N(6)	3.034		
O(2C)–Ba(1)–O(4A)	70.20	O(2C)–Ba(1)–N(1A)	68.34
O(2C)–Ba(1)–N(6A)	121.34	O(2C)–Ba(1)–O(3)	105.41
O(2C)–Ba(1)–O(2B)	159.39	O(2C)–Ba(1)–O(4)	129.48
O(2C)–Ba(1)–N(1)	109.46	O(2C)–Ba(1)–N(6)	65.21
O(2C)–Ba(1)–O(3A)	55.76	O(4A)–Ba(1)–N(1A)	70.64
O(4A)–Ba(1)–N(6A)	77.84	O(4A)–Ba(1)–O(3)	143.53
N(6)–Ba(1)–O(3A)	74.28	O(4A)–Ba(1)–O(4)	67.79
O(4A)–Ba(1)–N(1)	119.87	O(4A)–Ba(1)–N(6)	75.11
O(4A)–Ba(1)–O(3A)	125.05	N(1A)–Ba(1)–O(3)	74.21
N(1A)–Ba(1)–N(6A)	54.94	O(3)–Ba(1)–O(3A)	67.73
O(3)–Ba(1)–N(6)	137.62	N(1A)–Ba(1)–N(1)	168.49
N(1A)–Ba(1)–N(6)	129.1	N(1A)–Ba(1)–O(3A)	96.06
N(6A)–Ba(1)–O(3)	72.28	N(6A)–Ba(1)–O(3A)	137.62
N(6A)–Ba(1)–N(6)	147.28	N(6A)–Ba(1)–N(1)	129.12

Symmetry code for **1** A: $-x, 2-y, 1-z$; for **2** A: $0.5+x, -0.5-y, 0.5-z$; B: $x, -0.5-y, z$; C: $-0.5+x, y, 0.5-z$; D: $-0.5+x, -0.5-y, 0.5-z$; For **3** A: $-2-x, y, 1.5-z$; B: $-1-x, y, 1.5-z$; C: $-1+x, y, z$.

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

D–H···A	D–H	H···A	D···A	D–H···A
$C_{14}H_{24}MgN_{12}O_{11}$ (1)				
O(3)–H(3C)···O(1)#1	0.96	2.02	2.7451	130
O(4)–H(4B)···N(5)#2	0.96	2.14	3.0396	155
O(4)–H(4C)···O(2)#3	0.96	1.84	2.7102	149
O(6)–H(6C)···O(1)#4	0.85	2.25	3.005	149
$C_{14}H_{22}SrN_{12}O_{10}$ (2)				
O(3)–H(3A)···O(5)	0.85	2.11	2.8972	153
O(4)–H(4A)···O(5)#1	0.85	2.14	2.8503	141
O(5)–H(5A)···O(6)	0.85	2.14	2.9587	164
O(5)–H(5B)···O(6)#1	0.85	1.81	2.6192	158
O(6)–H(6C)···O(2)#2	0.85	1.84	2.6956	169
O(6)–H(6D)···N(5)#3	0.85	2.15	2.8631	141
$C_{14}H_{20}BaN_{12}O_9$ (3)				
O(3)–H(3C)···N(5)#1	0.91	2.02	2.9042	164
O(4)–H(4B)···O(1)#2	0.90	2.05	2.8958	158
O(4)–H(4C)···O(3)#3	0.88	2.06	2.8915	159
O(5)–H(5B)···O(1)	0.76	2.10	2.844	168

Symmetry codes for **1**: # 1: $0.5-x, 1.5+y, 0.5-z$; #2: $-0.5+x, 0.5+y, z$; #3: $0.5-x, 0.5+y, 0.5-z$; #4: $1-x, 1+y, 0.5-z$. For **2**: #1: $0.5+x, y, -0.5-z$; #2: $-0.5+x, y, -0.5-z$; #3: $-1+x, y, z$. For **3**: #1: $-2-x, 1-y, 1-z$; #2: $-1+x, y, z$; #3: $x, -1+y, z$.

Mo K α radiation ($\lambda = 0.071073$ Å). The intensity data were collected by the ω scan technique and were reduced using Crystal-Clear program [12,13]. An empirical absorption correction based on scans was applied. The structure was solved by the direct methods and refined by full matrix least-squares on F^2 using SHELXTL [14]. All

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