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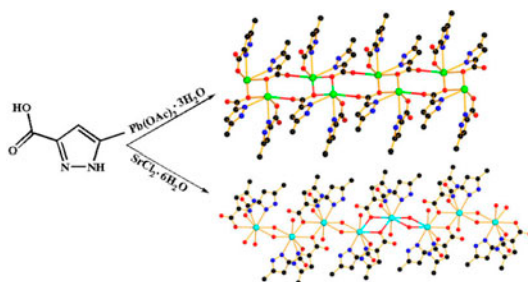
Synthesis, crystal structures, and luminescent properties of Pb(II) and Sr(II) coordination polymers constructed by 5-methyl-1H-pyrazole-3-carboxylic acid

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Two new 1D coordination polymers, $\{[\text{Pb}(\text{HMPCA})_2]\}_n$ (**1**), bridged by HMPCA^- , and $\{[\text{Sr}(\text{HMPCA})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (**2**), connected by the HMPCA^- and bridging waters, have been obtained via the reactions of H_2MPCA with metal salts.

Two new coordination polymers, $\{[\text{Pb}(\text{HMPCA})_2]\}_n$ (**1**) and $\{[\text{Sr}(\text{HMPCA})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (**2**) (H_2MPCA = 5-methyl-1H-pyrazole-3-carboxylic acid), have been synthesized and characterized by elemental analysis, IR spectroscopy, X-ray diffraction, and thermogravimetric analysis. Compound **1** forms a one-dimensional (1-D) chain, and a two-dimensional (2-D) supramolecular framework is constructed by hydrogen bonding. The HMPCA^- in **1** adopts two coordination modes, a N,O-chelate and a $\mu_3\text{-}\kappa\text{N}$, O: κO , O': $\kappa\text{O}'$ mode. The structure of **2** is a 1-D Sr–O–Sr chain built up by two waters bridging a pair of distronium $[\text{Sr}(\text{H}_2\text{O})(\text{HMPCA})(\mu_2\text{-HMPCA})]_2$ units, and the chains are further extended into a 2-D supramolecular layer via hydrogen bonds. In addition to a N,O-chelate, the HMPCA^- in **2** exhibit a third coordination mode, $\mu_2\text{-}\kappa\text{N}$, O: κO . The thermal decomposition and luminescent properties of **1** and **2** in the solid state have also been investigated.

Keywords: Lead(II); Strontium(II); 5-Methyl-1H-pyrazole-3-carboxylic acid; Crystal structure; Luminescent property

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1. Introduction

Considerable effort has been devoted to synthesis and characterization of coordination polymers because of their potential applications in gas adsorption, separation, optics, catalysis, lithium-ion batteries, and information storage [1–6]. A large number of coordination polymers containing N-heterocyclic carboxylic acids have been prepared and characterized [7–21], among which imidazolecarboxylic acid [7, 8], pyridinecarboxylic acid [9, 10] pyrimidinecarboxylic acid [11, 12], pyrazinecarboxylic acid [13, 14], and pyrazolecarboxylic acid [15–20] are the most used multifunctional ligands due to their strong coordination ability and multicoordination modes by N and O donors. These ligands coordinate to metal ions not only in a N,O-chelating fashion but also as μ_2^- , μ_3^- , μ_4^- , μ_5^- , and higher bridging connectors [9, 11, 16, 21]. Recently, we have been prepared several complexes with pyrazolecarboxylic acids, such as 3,4-pyrazoledicarboxylic acid [19], 3-methyl-1H-pyrazole-4-carboxylic acid, and 5-methyl-1H-pyrazole-3-carboxylic acid (H_2MPCA) [20]. For example, two monomeric complexes $[M(ImH)_2(HMPCA)_2 \cdot 2H_2O]$ ($M = Co, Ni$) ($ImH =$ imidazole), which are connected by intermolecular hydrogen bonds to form a three-dimensional supramolecular architecture with channels, were synthesized by reaction of H_2MPCA and ImH with $M(OAc)_2 \cdot 4H_2O$ ($M = Co, Ni$). However, research on the use of H_2MPCA as a bridging ligand to construct main group metal coordination polymers has not been undertaken. As a continuation of our studies in constructing new functional complexes containing N-heterocyclic carboxylic acids, we carried out reactions of H_2MPCA with the main group metal salts $Pb(OAc)_2 \cdot 3H_2O$ and $SrCl_2 \cdot 6H_2O$, and two coordination polymers $\{[Pb(HMPCA)_2]\}_n$ (**1**) and $\{[Sr(HMPCA)_2(H_2O)_2] \cdot H_2O\}_n$ (**2**) were isolated. In this article, the synthesis, crystal structures, and photoluminescent properties of **1** and **2** are described.

2. Experimental

2.1. Materials and methods

All solvents and starting materials for synthesis were purchased commercially and used as received. H_2MPCA was synthesized and purified by adopting the procedure in the literature [22] used to prepare 5-(4-methoxyphenyl)pyrazole-3-carboxylic acid, except 4-methoxyacetophenone was replaced by acetone. The C, H, and N elemental analyses were performed on a Perkin-Elmer 2400 Series II element analyzer. FTIR spectra were recorded on a Nicolet 460 spectrophotometer as KBr pellets. Luminescence spectra were recorded at room temperature on a Shimadzu RF-5301PC fluorescence spectrofluorometer. Powder X-ray diffraction (PXRD) studies were performed on an X-ray diffractometer (D/max 2500 PC, Rigaku) with $Cu-K\alpha$ radiation (1.5406 Å). Thermogravimetric analyses (TGA) were carried out on a Dupont thermal analyzer from room temperature to 800 °C under N_2 at a heating rate of 10 °C min^{-1} .

2.2. Preparation of $\{[Pb(HMPCA)_2]\}_n$ (**1**)

A solution of $Pb(OAc)_2 \cdot 3H_2O$ (0.0379 g, 0.1 mM) in water (3 mL) was added to a solution of H_2MPCA (0.0126 g, 0.1 mM) in 6 mL of a 1 : 1 (v : v) EtOH and water and stirred for 1 h. The resulting solution was evaporated at room temperature. Colorless crystals of **1** (0.0178 g, 78%) suitable for single-crystal X-ray diffraction analysis were obtained after

one day. Anal. Calcd for $C_{10}H_{10}N_4O_4Pb$ (%): C, 26.23; H, 2.19; N, 12.24. Found: C, 26.45; H, 2.62; N, 12.62. IR (KBr pellet, cm^{-1}): 3431(w), 3168(m), 3133(s), 3080(s), 2965(m), 2849(m), 1588(s), 1569(m), 1481(m), 1447(w), 1410(s), 1374(m), 1329(s), 1282(s), 1185(w), 1113(w), 1019(m), 1008(m), 883(w), 844(m), 825(s), 802(s), 681(s), 646(m), 554(m), 533(w), 447(m), 436(w).

2.3. Preparation of $\{[Sr(HMPCA)_2(H_2O)_2] \cdot H_2O\}_n$ (**2**)

A solution of $SrCl_2 \cdot 6H_2O$ (0.0226 g, 0.1 mM) in water (3 mL) was added to a solution containing H_2MPCA (0.0126 g, 0.1 mM) and ImH (0.0170 g, 0.25 mM) in EtOH (4 mL). The resulting colorless solution was allowed to stand at ambient temperature for two weeks to afford colorless crystals (0.0143 g, 73%). Anal. Calcd for $C_{10}H_{16}SrN_4O_7$ (%): C, 30.62; H, 4.08; N, 14.29. Found: C, 30.15; H, 4.17; N, 14.48. IR data (cm^{-1} , KBr pellet): 3590(s), 3296(s), 3129(s), 3102(s), 1584(s), 1575(s), 1488(s), 1422(s), 1374(m), 1346(s), 1294(m), 1185(m), 1126(w), 1029(m), 1005(m), 838(w), 824(w), 792(m), 716(w), 694(w), 680(m), 655(m), 614(w), 547(w), 478(w), 439(m).

2.4. X-ray crystallography

Single-crystal X-ray diffraction data were collected on a Bruker Smart Apex II CCD diffractometer at 296(2) K (**1**) and 293(2) K (**2**). Reflection intensities were measured using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using the SHELXS of the SHELXTL package and refined with SHELXL [23]. Anisotropic thermal factors were assigned to all non-hydrogen atoms. Hydrogens attached to C were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.2 times U_{eq} of the parent. Hydrogens bonded to O or N were first located in difference Fourier maps and then fixed in these sites

Table 1. Crystal structure and refinement parameters of **1** and **2**.

Compound	1	2
Empirical formula	$C_{10}H_{10}PbN_4O_4$	$C_{10}H_{16}SrN_4O_7$
Formula mass	457.41	391.89
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.0663(14)	8.298(2)
b (Å)	7.2322(8)	8.503(2)
c (Å)	14.0689(15)	11.903(3)
α (°)	90.00	84.599(6)
β (°)	99.444(2)	76.468(6)
γ (°)	90.00	66.923(5)
V (Å ³)	1211.1(2)	751.2(3)
Z	4	2
D_c (g cm ⁻³)	2.509	1.733
μ (Mo $K\alpha$)/mm ⁻¹	1.3948	0.363
$F(000)$	848	396
Reflections collected	8218	3936
Independent reflections	3207	2588
Goodness-of-fit on F^2	1.082	1.114
$R_1, wR_2 [I > 2\sigma(I)]$	0.0296, 0.0746	0.0735, 0.2164
R_1, wR_2 (all data)	0.0377, 0.0961	0.0848, 0.2410
Largest diff. peak and hole (e Å ⁻³)	1.05, -1.25	2.23, -2.57

and included in the refinement. Crystallographic data parameters for structural analyses are summarized in table 1.

3. Results and discussion

3.1. Synthesis

For a systematic investigation of the relationship between H₂MPCA and main group metal complexes, our strategy was to obtain crystals of their complexes suitable for X-ray diffraction. Reaction of an aqueous solution of Pb(OAc)₂·3H₂O with an equimolar amount of H₂MPCA in H₂O–EtOH afforded a one-dimensional (1-D) coordination polymer **1**. The crystals of **2** were generated by evaporation of EtOH–H₂O solution of SrCl₂·6H₂O, ImH, and H₂MPCA in a molar ratio 1 : 2.5 : 1. Only a powder of **2** was obtained under the same reaction conditions but in the absence of ImH (figure S4). ImH may play a role in the crystallization of **2**. These complexes are stable in air and insoluble in water and common organic solvents. Elemental analyses of **1** and **2** were consistent with the formulas. The identities of **1** and **2** were confirmed by X-ray crystallography.

3.2. Infrared spectrum

In IR spectra of both **1** and **2** (figure S1, see online supplemental material at <http://dx.doi.org/10.1080/00958972.2013.879983>), the absence of absorption peaks around 1730 cm⁻¹ shows that all carboxylic groups are deprotonated [24]. Strong peaks at 1588 cm⁻¹ (**1**) and 1584 cm⁻¹ (**2**), and 1410 cm⁻¹ (**1**) and 1422 cm⁻¹ (**2**), may be assigned to the ν_{as}(OCO) and ν_s(OCO) stretches of HMPCA⁻ ligand [24, 25]. A strong peak at 3600–3000 cm⁻¹ in the spectrum of **2** is assigned as the characteristic peak of the OH vibration, confirming the presence of water in **2**. These assignments are supported by the X-ray crystal structure analysis.

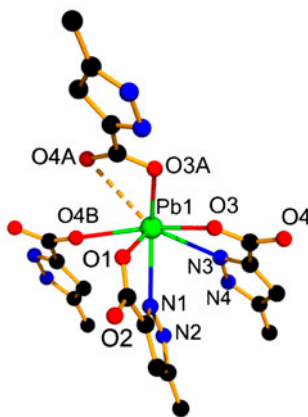


Figure 1. The coordination environment of Pb²⁺ in **1**. The hydrogens are omitted for clarity. Symmetry codes: A: 1 - x, -y, 1 - z; B: x, 1 + y, z.

3.3. Crystal structure description of **1**

X-ray crystal structure analysis revealed that **1** crystallized in the monoclinic system space group $P2_1/c$. The asymmetric unit consists of one Pb^{2+} and two HMPCA^- . Each Pb(II) is six-coordinate by carboxylates O(1), O(3), O(3A), and O(4B) and pyrazoles N(1) and N(3) from 4 individual HMPCA^- ligands to furnish a hemidirected $[\text{PbO}_4\text{N}_2]$ geometry (figure 1). As shown in figure S2, all the O and N donors cluster to one side of the Pb^{2+} leaving an “open” coordination site approximately between O(3) and O(4B) to accommodate the stereochemically active 6s lone pair. This hemidirected stereochemistry is common in other Pb(II) complexes [26]. “Primary bonds” and “secondary bonds” have been used to describe the coordination environment of Pb^{2+} [27]. The Pb–N bond distances (2.599(4)–2.795(4) Å) and Pb–O bond distances (2.372(4)–2.738(4) Å) are primary bonds (table 2). The Pb(1)⋯O(4A) distance of 3.244(4) Å (dashed lines in figure 1) is longer than the sum of the ionic radii but significantly shorter than the sum of the van der Waals radii (3.54 Å) [28]. This bond can be classified as a secondary bond and can be explained by the presence of an active lone electron pair in the proximity of O(4A). If the Pb(1)⋯O(4A) bond is taken into account, then the geometry around Pb(1) can be described as a seven-coordinate $[\text{PbO}_5\text{N}_2]$ geometry. The HMPCA^- ligand in **1** adopts two coordination modes: coordinating to Pb^{2+} in a N,O-chelating fashion as a five-membered chelate ring through carboxylate O(1) and its adjacent N(1) in the pyrazole ring [scheme 1(a) and figure 1] and coordinating to Pb^{2+} through a $\mu_3\text{-}\kappa\text{N, O:}\kappa\text{O, O':}\kappa\text{O'}$ bridging mode [scheme 1(b)], which links the Pb^{2+} cations into a $[\text{Pb}(\text{HMPCA})(\mu_2\text{-HMPCA})]_2$ unit via the carboxylate O(3) and O(4), as shown in figure 2. In addition, O(3) bridges a second Pb^{2+} , resulting in the formation of a centrosymmetric Pb_2O_2 unit with a Pb(1)⋯Pb(1A) distance of 4.212(4) Å. This distance is somewhat shorter than that in $[\text{Pb}(\text{HMIDC})]_n$ (4.372 Å, H_3MIDC = 2-methyl-1H-imidazole-4,5-dicarboxylic acid) [29] and $[\text{Pb}(\text{INO})\text{Cl}]$ (4.307 Å, HINO = isonicotinic acid N-oxide) [30], and significantly shorter than the sum of the van der Waals radii (4.6 Å). This indicates that there are weak Pb⋯Pb contacts within these Pb_2O_2 dinuclear units. In the central Pb_2O_2 ring of **1**, the two Pb–O bond distances are inequivalent with Pb(1)–O(3) 2.433(3) Å and Pb(1)–O(3A) 2.552(3) Å. The mean Pb–O bond distance of 2.492(3) Å is a little shorter than that in the similar Pb_2O_2 rings in $[\text{Pb}(\text{INO})\text{Cl}]$ (2.6703(3) Å) [30]. The mean Pb–N bond distance 2.697(4) Å is close to that in $[\text{Pb}(\text{H}_2\text{tpaa})\text{Cl}]$ (2.702(6) Å, H_2tpaa = $\alpha, \alpha', \alpha''$ -nitrotri(6-methyl-2-pyridinecarboxylic acid) [28], but somewhat longer than that found in $[\text{Pb}(\text{HMIDC})]_n$ (2.548(6) Å) [29].

The combination of $[\text{Pb}(\text{HMPCA})(\mu_2\text{-HMPCA})]_2$ and Pb_2O_2 rings gives rise to dileded units propagating approximately along the *b*-axis in the crystal and generating an infinite

Table 2. Selected bond distances (Å) and angles (°) in **1**.

Pb(1)–O(1)	2.372(4)	Pb(1)–N(1)	2.599(4)
Pb(1)–O(3)	2.433(3)	Pb(1)–O(4B)	2.738(4)
Pb(1)–O(3A)	2.552(3)	Pb(1)–N(3)	2.795(4)
O(1)–Pb(1)–O(3)	79.49(12)	O(3A)–Pb(1)–O(4B)	110.48(14)
O(1)–Pb(1)–O(3A)	72.25(12)	N(1)–Pb(1)–O(4B)	82.61(12)
O(3)–Pb(1)–O(3A)	64.70(12)	O(1)–Pb(1)–N(3)	120.16(11)
O(1)–Pb(1)–N(1)	65.34(12)	O(3)–Pb(1)–N(3)	62.22(11)
O(3)–Pb(1)–N(1)	89.26(12)	O(3)–Pb(1)–N(3A)	120.12(10)
O(3)–Pb(1)–N(1A)	134.47(12)	N(1)–Pb(1)–N(3)	69.79(12)
O(1)–Pb(1)–O(4B)	82.45(12)	O(4B)–Pb(1)–N(3)	128.39(10)
O(3)–Pb(1)–O(4B)	161.93(13)		

Note: Symmetry codes: A: 1 – *x*, 2 – *y*, 1 – *z*; B: *x*, 1 + *y*, *z*.

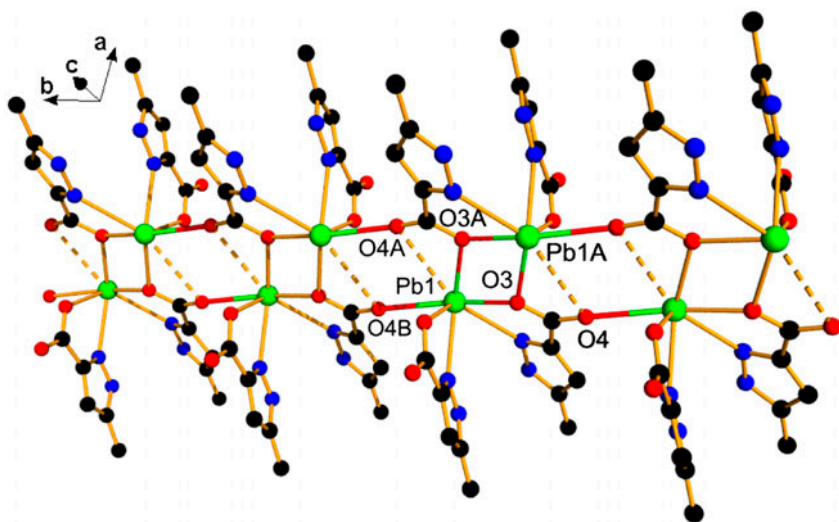


Figure 2. The 1-D chain of **1**. The hydrogens are omitted for clarity. Symmetry codes: A: $1-x, -y, 1-z$; B: $x, 1+y, z$.

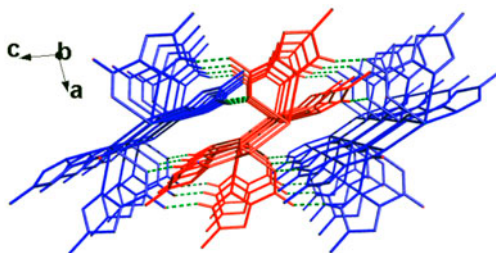


Figure 3. The 2-D supramolecular structure of **1** viewed along the *b*-axis. Hydrogen bonds are indicated by dash lines and the adjacent chains are shown in different colors for clarity.

1-D chain. These 1-D coordination chains are then extended into a two-dimensional (2-D) structure by two kinds of intermolecular hydrogen bonding interactions, $N(2)-H(2A)\cdots O(2)^i$ and $N(4)-H(4A)\cdots O(1)^i$ [symmetry code: $^i x, 1/2 - y, -1/2 + z$] (figure 3). Both of the hydrogen bonds are normal since the distances are 2.754(7)–2.811(6) Å and the bond angles are 156–170° (table 3).

Table 3. Bond distances (Å) and angles (°) of hydrogen bonds in **1**.

D–H⋯A	D–H	H⋯A	D⋯A	D–H⋯A
$N(2)-H(2A)\cdots O(2)^i$	0.86	1.94	2.751(5)	156
$N(4)-H(4A)\cdots O(1)^i$	0.86	1.95	2.806(5)	171
$C(6)-H(6C)\cdots O(4)^{ii}$	0.96	2.43	3.345(8)	158

Note: Symmetry codes: (i) $x, 5/2 - y, -1/2 + z$; (ii) $x, 3/2 - y, -1/2 + z$.

3.4. Crystal structure description of 2

X-ray crystal structure analysis revealed that **2** crystallized in the triclinic system space group $P\bar{1}$. The asymmetric unit of **2** contains one Sr^{2+} , two HMPCA^- ligands, two coordinated waters, and a solvent water. As shown in figure 4, Sr(1) is eight-coordinated by N(1), N(3), O(1), and O(3) from two HMPCA^- ligands, one carboxylate O(3B) from a third HMPCA^- ligand, and O(5), O(5B), and O(6) from three waters. The Sr coordination sphere is a distorted square antiprism geometry, in which the sets of atoms O(3), N(3), O(5), O(6), and O(1), O(3B), O(5B), N(1) form two approximate squares (figure S3). The crystallographically equivalent Sr(1) and Sr(1A) are linked by two μ_2 -O (O(3) and O(3A)) from carboxylates of HMPCA^- , resulting in the formation of a O-bridged, centrosymmetric $[\text{Sr}(\text{H}_2\text{O})(\text{HMPCA})(\mu_2\text{-HMPCA})]_2$ unit with a Sr(1)··Sr(1A) distance of 4.268(2) Å. This distance is comparable to that in $[\text{Sr}_2\text{L}(\text{H}_2\text{O})_4]_n \cdot n\text{H}_2\text{O}$ (4.265(1) Å, $\text{H}_4\text{L} = 2,4$ -dihydroxy-1,5-benzenedisulfonic acid) [31], but a little longer than that in $[\text{Sr}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})]$ (4.1691(2) Å, $\text{H}_4\text{dhtp} = 2,5$ dihydroxyterephthalic acid) [32]. In this Sr_2O_2 ring, the two Sr–O bond distances are nearly equivalent with Sr(1)–O(3) 2.636(5) Å and Sr(1)–O(3A) 2.598(4) Å. The mean Sr–O bond length of 2.617(4) Å is comparable to that in the similar Sr_2O_2 ring in $\text{Sr}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})$ (2.6814(13) Å) [32]. The mean Sr–N bond length 2.709(5) Å is close to that in $[\text{SrL}'_2(\text{H}_2\text{O})_2]$ (2.707(1) Å, $\text{L}' = 2$ -ethyl-4,5-imidazoledicarboxylate) [33], but a little shorter than that found in $[\text{Sr}(\text{H}_3\text{pdc})(\text{H}_2\text{pdc})_2(\text{H}_2\text{O})_3]_2 \cdot 2(\text{H}_3\text{pdc}) \cdot 4\text{H}_2\text{O}$ (2.682(3) Å, $\text{H}_3\text{pdc} = 3,5$ -pyrazoledicarboxylic acid) [34]. The $[\text{Sr}(\text{H}_2\text{O})(\text{HMPCA})(\mu_2\text{-HMPCA})]_2$ dimers are additionally bridged by two waters, O(5) and O(5B), with equivalent Sr–O bond distances of 2.717(5) Å. In this way, an infinite 1-D Sr–O–Sr chain along the a -axis is formed, as shown in figure 5. This is different from the 1-D coordination polymer **1**, in which the 1-D chains are formed by bridging HMPCA^- . The Sr(1)··Sr(1B) distance is 4.518(1) Å, close to that in the corresponding Sr_2O_2 ring of $[\text{Sr}(2,5\text{-pzdc})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}]$ (4.474(2) Å, 2,5-pzdc = pyrazine-2,5-dicarboxylic acid) [35], but slightly longer than the Sr(1)··Sr(1A) distance, consistent with the fact that the average Sr–O water bond distance is slightly longer than the average carboxylate Sr–O distance (table 4). The mean water Sr–O bond distance is close to the values observed in other Sr(II) complexes containing N-heterocyclic carboxylic acids, such as $[\text{Sr}(2,5\text{-pzdc})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}]$ (2.681(3) Å) [35] and $[\text{Sr}_2(2,6\text{-pzdc})_2(\text{H}_2\text{O})_7 \cdot 1.5\text{H}_2\text{O}]$ (2.690(3) Å, 2,6-pzdc = pyrazine-2,6-dicarboxylic acid) [36]. HMPCA^- in **2** exhibits two kinds of coordination modes, one as a N,O-chelate [scheme 1(a)] through O(1) and N(1), and the other as a

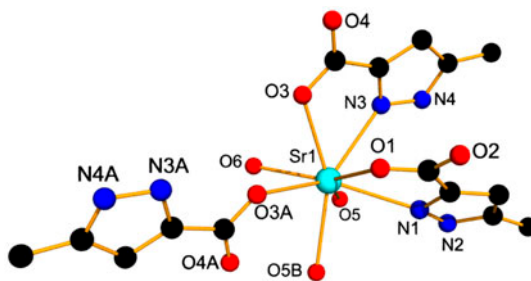


Figure 4. The coordination environment of Sr(II) in **2**. Symmetry codes: A: $1-x, 1-y, -z$; B: $-x, 1-y, -z$.

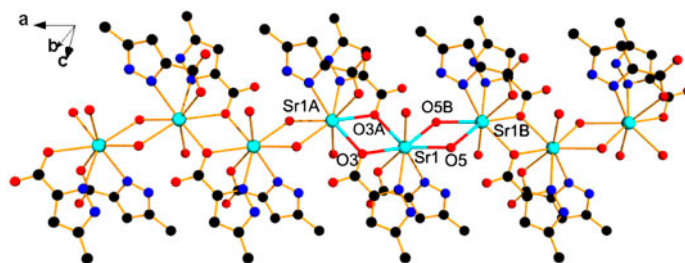


Figure 5. The 1-D chain of **2**, with 1-D Sr–O–Sr connectivity. Hydrogens and solvent water are omitted for clarity.

Table 4. Selected bond distances (Å) and angles (°) in **2**.

Sr(1)–N(1)	2.694(5)	Sr(1A)–O(3)	2.598(4)
Sr(1)–N(3)	2.725(6)	Sr(1)–O(5)	2.717(5)
Sr(1)–O(1)	2.576(5)	Sr(1)–O(5B)	2.717(5)
Sr(1)–O(3)	2.636(5)	Sr(1)–O(3A)	2.598(4)
Sr(1)–O(6)	2.534(5)		
O(1)–Sr(1)–O(5B)	110.69(15)	O(3)–Sr(1)–N(3)	61.68(15)
N(1)–Sr(1)–O(5B)	80.16(16)	N(1)–Sr(1)–N(3)	73.75(17)
O(6)–Sr(1)–O(5)	73.10(15)	O(5B)–Sr(1)–N(3)	143.88(15)
O(3A)–Sr(1)–O(5)	135.75(15)	O(5)–Sr(1)–N(3)	83.44(16)
N(1)–Sr(1)–O(5)	79.89(15)	O(6)–Sr(1)–O(1)	144.66(15)
O(6)–Sr(1)–N(3)	104.49(17)	O(6)–Sr(1)–O(3A)	72.33(15)
O(1)–Sr(1)–N(3)	78.65(17)	O(1)–Sr(1)–O(3A)	79.57(14)
O(3A)–Sr(1)–N(3)	131.69(15)	O(6)–Sr(1)–O(3)	78.41(15)
O(1)–Sr(1)–O(3)	72.30(15)	O(3A)–Sr(1)–O(3)	70.76(16)
O(6)–Sr(1)–N(1)	152.92(17)	O(1)–Sr(1)–N(1)	62.31(15)
O(3A)–Sr(1)–N(1)	129.58(16)	O(3)–Sr(1)–N(1)	121.02(15)
O(6)–Sr(1)–O(5B)	87.70(16)	O(3A)–Sr(1)–O(5B)	84.31(14)
O(3)–Sr(1)–O(5B)	154.12(15)	O(1)–Sr(1)–O(5)	141.32(15)
O(3)–Sr(1)–O(5)	126.99(14)	O(5B)–Sr(1)–O(5)	67.53(17)

Note: Symmetry codes: A: $1-x, 1-y, -z$; B: $-x, 1-y, -z$.

μ_2 - κ N, O: κ O mode, coordinated to two Sr²⁺ through O(3) and N(3) [scheme 1(c)]. As shown in scheme 1(c), O(3) of the carboxylate is used for bonding, the other one is inactive. Additionally, **2** contains multiple hydrogen bonds between coordinated waters, solvent water, O and N from HMPCA[−]. As listed in table 5, the O–H \cdots O hydrogen bond distances

Table 5. Bond distances (Å) and angles (°) of hydrogen bonds in **2**.

D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H \cdots A
N(2)–H(2) \cdots O(4) ⁱ	0.86	2.55	3.246(9)	138
N(2)–H(2) \cdots O(6) ⁱⁱ	0.86	2.30	2.943(9)	132
N(4)–H(4) \cdots O(7) ⁱⁱⁱ	0.86	1.96	2.794(10)	165
O(5)–H(5X) \cdots O(2) ^{iv}	0.85	1.86	2.695(7)	168
O(5)–H(5Y) \cdots O(4) ⁱ	0.85	2.02	2.726(8)	140
O(6)–H(6X) \cdots O(2) ^{iv}	0.85	1.97	2.688(8)	142
O(6)–H(6Y) \cdots O(1) ^v	0.86	1.87	2.721(8)	178
O(7)–H(7Y) \cdots O(4) ^{vi}	0.80	1.92	2.708(9)	171

Note: Symmetry codes: (i) $-1+x, y, z$; (ii) $-x, 1-y, -z$; (iii) $-x, 1-y, 1-z$; (iv) $x, -1+y, z$; (v) $1-x, 1-y, -z$; (vi) $1-x, 1-y, 1-z$.

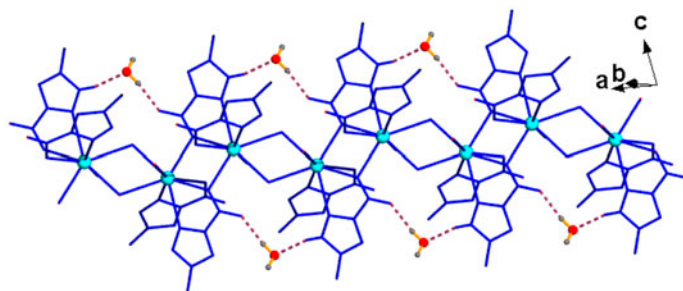


Figure 6. The hydrogen bond interactions between solvent water molecules and HMPCA⁻ anions in the 1-D chain. Only hydrogens involved in the hydrogen bonds are shown. Hydrogen bonds are indicated by dashed lines; the 1-D chain is shown in the same color.

and angles are 2.688(8)–2.726(8) Å and 140–178°, respectively, while the N–H···O distances and angles are 2.794(10)–3.246(9) Å and 132–165°, respectively. The solvent waters are embedded in the 1-D coordination chain via two hydrogen bonds N(4)–H(4)···O(7)ⁱⁱⁱ and O(7)–H(7Y)···O(4)^{vi} (figure 6). Finally, the 1-D chains are packed along the *b*-axis through the remaining O–H···O and N–H···O interactions to generate a 2-D supramolecular layer as illustrated in figure 7.

The experimental PXRD pattern for each complex correlates well with its simulated one generated from single-crystal X-ray diffraction data (figure S4), confirming the phase purity of the bulk materials.

3.5. Thermal stability

TGA were carried out to study thermal behaviors of **1** and **2** (figure S5). For **1**, the TGA showed one major loss stage between 283 and 793 °C, which corresponds to loss of two HMPCA⁻ ligands. The pyrolysis product was PbO (Calcd, 48.80%; found, 48.90%). These data showed that **1** kept its integrity up to 283 °C. For **2**, the first weight loss of 13.88% between 63 and 135 °C is attributed to the loss of three waters (Calcd 13.79%). The second degradation stage was from 285 to 428 °C with mass loss of 32.08%, corresponding to the

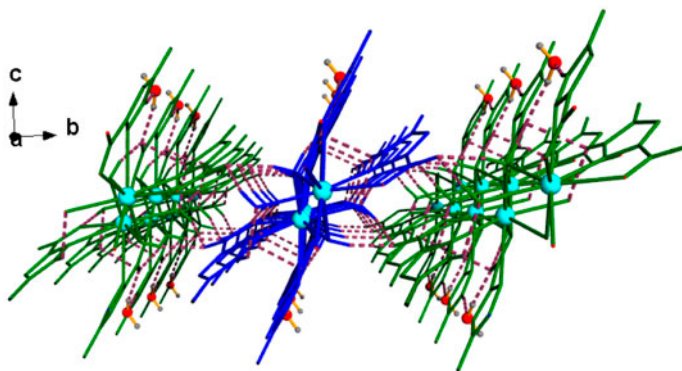


Figure 7. The 2-D supramolecular structure of **2** viewed down the *a*-axis. Hydrogen bonds are indicated by dash lines; adjacent chains are shown in different colors for clarity.

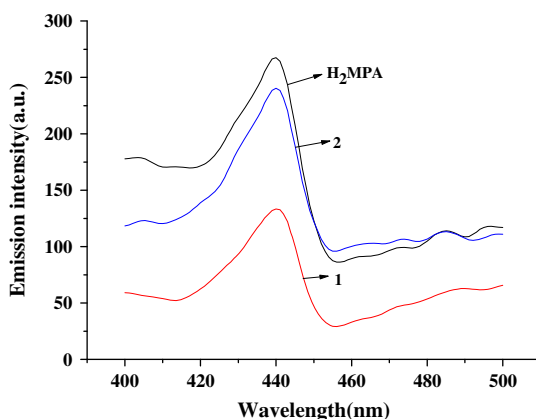
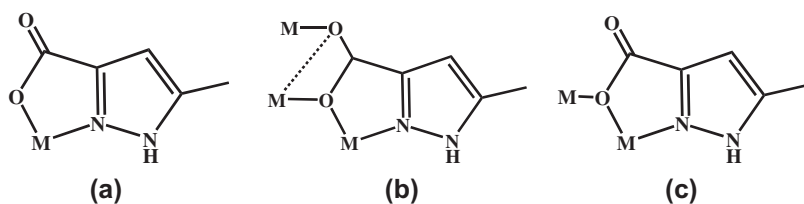


Figure 8. Solid-state emission spectra for **1**, **2**, and H₂MPCA ($\lambda_{\text{ex}} = 331$ nm) at room temperature.



Scheme 1. Different coordination modes of H₂MPCA in **1** and **2**.

loss of HMPCA⁻ (Calcd 31.92%). Above 428 °C, the remaining material gradually decomposed, but this degradation was not completed by 800 °C.

3.6. Luminescent properties

The solid-state luminescent properties of free H₂MPCA, **1**, and **2** were investigated at room temperature as shown in figure 8. H₂MPCA, **1**, and **2** exhibited blue fluorescence with emission maxima at 440, 441, and 441 nm, respectively, upon excitation at 331 nm. The emission of free ligand may be attributed to $\pi \rightarrow \pi^*$ transitions. The emission bands of **1** and **2** are similar to that of the free ligand in terms of position and band shape, which indicates that these emissions should also originate from $\pi \rightarrow \pi^*$ transitions of the ligand. Moreover, the emission intensity of **1** is obviously weaker than that of the free ligand, which may be attributed to fluorescence quenching of the triplet state of Pb²⁺ [29].

4. Conclusion

We have synthesized and characterized by X-ray diffraction two new coordination polymers, {[Pb(HMPCA)₂]}_n (**1**) and {[Sr(HMPCA)₂(H₂O)₂]·H₂O}_n (**2**), by reaction of corresponding metal salts with H₂MPCA. The results show that the HMPCA⁻ in **1** and **2** adopt

three kinds of coordination. Although HMPCA⁻ is found as a N,O-chelating ligand [scheme 1(a)] in several mononuclear transition metal complexes, [M(ImH)₂(HMPCA)₂·2H₂O] (M = Co, Ni) [20] Co(HMPCA)₂(H₂O)₂ [37], [Cu(HMPCA)₂(H₂O)]·3H₂O [38], [Cu(phen)(HMPCA)₂]·6H₂O (phen = 1,10-phenanthroline) [39], and [VO(pzH)(HMPCA)₂]·4H₂O (pzH = pyrazole) [40], and the μ_2 - κ N, O: κ O mode [scheme 1(c)] adopted in **2** is present in {[Cu(HMPCA)₂](H₂O)}_n [37] and the dinuclear complex [(TMPzA)Co(μ -HZPC)Co(HMPCA)(H₂O)₂](ClO₄)₃ (TMPzA = tris(3,5-bimethyl-pyrazolymethyl)amine) [41], a μ_3 -HMPCA⁻ [scheme 1(b)] in **1** is unprecedented in metal complexes. Polymers **1** and **2** are 1-D chain structures containing dinuclear units, which are further assembled into 2-D structures through intermolecular hydrogen bonds. In **1**, only HMPCA⁻ bridge, while in **2**, HMPCA⁻ and waters bridge metal ions, resulting in a 1-D chain structure. **1** and **2** displayed blue fluorescence in the solid state at room temperature.

Supplementary material

Figures of the IR spectra, metal coordination geometries, experimental and simulated PXRD patterns, and TG curves of **1** and **2**. Sentence on cif file deposition at the Cambridge database.

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