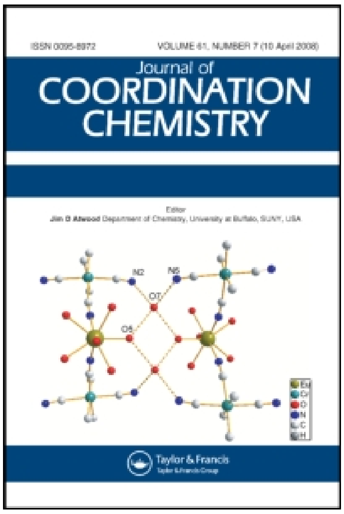

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A 1D coordination polymer $\{Pb[C_6H_4(COO)_2][phen]\}_n$ with strong blue fluorescent emission

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The hydrothermal reaction of 1,3-dicyanobenzene, 1,10-phenanthroline (phen) and $Pb(CH_3COO)_2$ yields a new 1D coordination polymer, $\{Pb[C_6H_4(COO)_2][phen]\}_n$. The 1,3-benzenecarboxylate anion found in the final product was generated *in situ* during the synthesis by hydrolysis of 1,3-dicyanobenzene. X-ray diffraction shows that complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, $a = 7.5442(2)$ Å, $b = 9.7962(3)$ Å, $c = 13.1505(4)$ Å, $\alpha = 69.739(2)$ Å, $\beta = 80.597(2)$ Å, $\gamma = 71.377(2)$ Å, $v = 862.48(4)$ Å^3, $Z = 2$, $D_c = 2.124$ Mg m^{-3}. Complex **1** emits strong blue fluorescent light (λem(max) = 482.4 nm) when excited by UV light in the solid state at room temperature.

Keywords: Crystal structure; Coordination polymer; Hydrothermal syntheses; Fluorescence; 1,3-Benzenecarboxylate ligand

1. Introduction

The construction of new metal-organic hybrid compounds are of importance, owing to intriguing structural motifs and potential applications in catalysis, medicine, host-guest chemistry and photomaterials, electromaterials and magnetic materials [1–4]. Metal coordination polymers have been reported for Cu^{2+} [5], Zn^{2+} [6], Mn^{2+} [7], Fe^{2+} [8], Nd^{2+} and Gd^{3+} [9], Eu^{3+} and Sm^{3+} [10] with 1,3-benzenedicarboxylic acid, a type of angular bridging ligand. We utilized 1,3-dicyanobenzene as a precursor to synthesize a 1D Ca^{2+} coordination polymer [11]. Most supramolecular frameworks are not bridged by just one ligand, but two or more ligands are usually employed. Multi-dentate ligands containing N– or O–donors used to bind metal centers, altering the dimensionality of these metal-organic hybrid compounds [12, 13]. In this article, we report the hydro-thermal synthesis and structural characterization of $\{Pb[C_6H_4(COO)_2][phen]\}_n$ (**1**), which has a supramolecular framework (see Scheme 1). To the best of our knowledge, **1** represents the first metal-organic supramolecular framework composed of Pb^{2+} and phen and 1,3-benzenecarboxylate.

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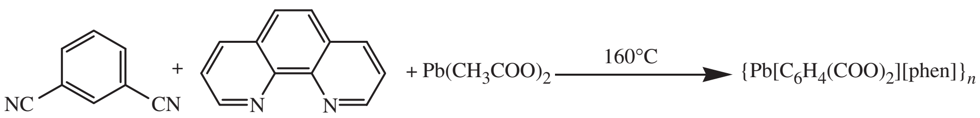

Scheme 1. The formation of **1**.

2. Experimental

2.1. *Materials and physical measurements*

1,3-Dicyanobenzene was purchased from Acro Chemical Co. All other chemicals were of reagent grade and used as purchased without further purification. C, H and N data were obtained using an American PE 2400II CHNS/O elemental analyzer. Infrared spectra were measured from KBr pellets using a Nicolet 5DXB system. Excitation and emission spectra for the solid state of complex **1** were measured with an F-4500 FL spectrophotometer at room temperature.

2.2. *Preparation of complex* 1

$\{Pb[C_6H_4(COO)_2][phen]\}_n$ (**1**). An aqueous mixture (15 mL) containing 1,3-dicyanobenzene (2 mmol, 0.256 g), 1,10-phenanthroline (0.5 mmol, 0.1000 g), and $Pb(CH_3COO)_2$ (0.5 mmol, 0.1900 g) was placed in a Teflon-lined stainless steel vessel (25 mL). Ethanol (5.0 mL) was added to the mixture. The vessel was sealed and heated to 160°C for 7 days. Upon cooling to room temperature, colorless block crystals of **1** were obtained. Anal. Calcd for $C_{20}H_{12}N_2O_4Pb$: C, 43.51; H, 2.18; N, 5.08. Found: C, 43.49; H, 2.20; N, 5.10. IR data: (KBr pellets, cm^{-1}), 3399(s), 2426(w), 1625(s), 1582(m), 1546(s), 1518(s), 1425(s), 1384(s), 1224(w), 1143 (w), 1104(w), 1051(w), 870(m), 848(m), 754(m), 727(s), 645(m).

The IR spectrum of **1** shows characteristic peaks for COO^-. The medium peak at 2200 cm^{-1} of ν(C–N) disappears, indicating that the two cyano groups of 1,3-dicyanobenzene were hydrolyzed completely. A strong peak at 1625 cm^{-1} indicates that the carboxylic acid is deprotonated (ca 1700 cm^{-1}, in free 1,3-benzenecarboxylic acid), implying that 1,3-dicyanobenzene has been hydrolyzed into 1,3-benzenecarboxylate.

2.3. *Crystal structure determination*

The X-ray single crystal data collection for **1** was performed on a Bruker Smart CCD diffractometer equipped with a graphite monochromator Mo-Kα radiation ($\lambda = 0.71073$ Å). Multi-scan absorption correction was applied using the SADABS program. The structure was solved by direct methods using the SHELXS-97 program. Refinement on F^2 was performed using SHELXS-97 by full-matrix least-squares with anisotropic parameters for all non-hydrogen atoms. The hydrogen atoms were generated geometrically.

Table 1. Summary of crystallographic data for **1**.

Parameter	
Formula	$C_{20}H_{12}N_2O_4Pb$
Formula weight	551.51
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.5442(2)
b (Å)	9.7962(3)
c (Å)	13.1505(4)
α (°)	69.739(2)
β (°)	80.597(2)
γ (°)	71.377(2)
Z	2
F (000)	520
D_c ($Mg\,m^{-3}$)	2.124
T (K)	293(2)
Reflections collected	7562
Independent reflections	3302
Goodness-of-fit on F^2	1.092
Final R index [$I > 2\sigma(I)$]	$R_1 = 0.0197$, $wR_2 = 0.0472$

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Pb(1)–O(1)	2.627(3)	Pb(1)–O(2)	2.468(3)
Pb(1)–N(1)	2.684(3)	Pb(1)–N(2)	2.521(3)
Pb(1)–O(3)#1	2.710(3)	Pb(1)–O(4)#1	2.390(3)
O(4)#1–Pb(1)–O(1)	130.94(9)	O(2)–Pb(1)–N(2)	74.90(9)
O(4)#1–Pb(1)–O(2)	82.65(9)	O(4)#1–Pb(1)–N(2)	75.23(10)
O(2)–Pb(1)–O(1)	51.47(9)	N(2)–Pb(1)–O(1)	76.57(11)
O(4)#1–Pb(1)–N(1)	122.02(10)	O(2)–Pb(1)–N(1)	119.71(9)
N(2)–Pb(1)–N(1)	63.17(10)	O(1)–Pb(1)–N(1)	77.11(10)
O(4)#1–Pb(1)–O(3)#1	50.91(8)	O(2)–Pb(1)–O(3)#1	131.62(8)
N(2)–Pb(1)–O(3)#1	80.09(10)	O(1)–Pb(1)–O(3)#1	154.05(10)

Symmetry transformations used to generate equivalent atoms: #1 $x+1$, $y-1$, z; #2 $x-1$, $y+1$, z.

3. Results and discussion

3.1. *Crystal structure of (1)*

The crystal data of **1** are listed in table 1 and selected bond distances and angles are listed in table 2. In the asymmetric unit of **1**, there is one crystallographically independent Pb(II) ion, and each Pb(II) is coordinated to four oxygen atoms, two oxygen atoms (O1 and O2) from one tetradentate 1,3-benzenecarboxylate ligand, two oxygen atoms (O3a and O4a) from another tetradentate 1,3-benzenecarboxylate ligand, as well as two nitrogen atoms (N1 and N2) from one phen to complete a six-coordinated geometry, as shown in figure 1. Pb(II) is located in the center of the distorted octahedron formed by these six atoms. The Pb(1)–O distances range from 2.390 to 2.710 Å, the mean bond Pb(1)–O distance is 2.549 Å, while O–Pb(1)–O bond angles are in the range 51.47(9)–154.05°(10). In **1**, 1,3-benzenecarboxylate has one coordination mode; each tetradentate 1,3-benzenecarboxylate anion connects two Pb(II) ions in chelating and bridging coordination, see figure 1. In the 1D chain, the 1,3-benzenecarboxylate ligands coordinated to Pb(II) ions in a chelating mode by

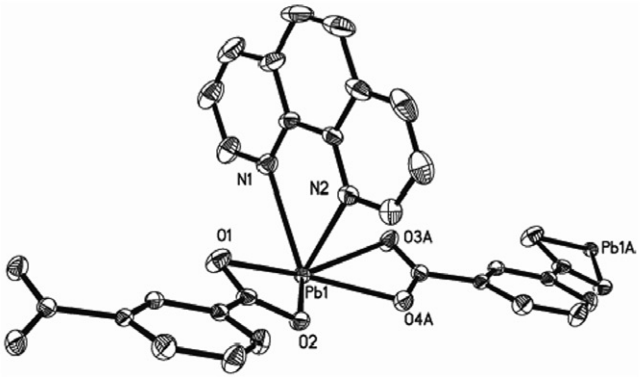

Figure 1. The coordination environment of Pb(II) in **1**. All hydrogen atoms are omitted for clarity.

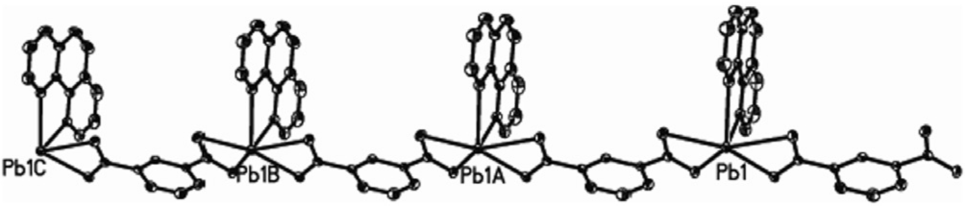

Figure 2. 1D chain of **1**.

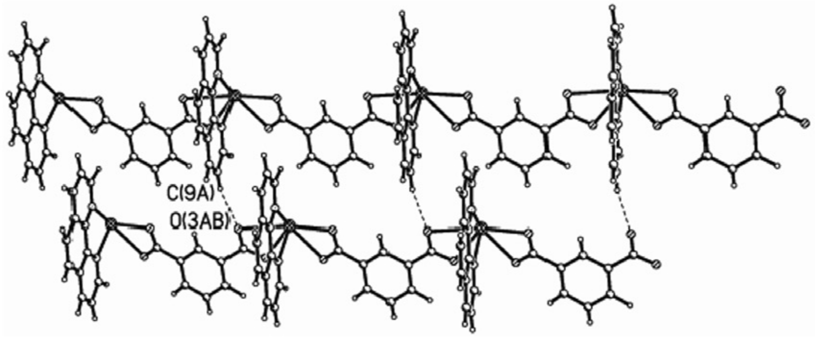

Figure 3. 2D network of **1**. Hydrogen bonds are shown in dotted line.

deprotonated carboxylate groups, the distance of neighboring Pb(II) ions is 10.280 Å, while phen molecules are parallel to each other and locate on one side of the 1D chain, see figure 2. In fact, there is one type of hydrogen bond (C–H $\cdots$ O) between hydrogen atoms of the aromatic ring of 1,3-benzenecarboxylate anions and coordinated carboxylate oxygen atoms from adjacent chains, see figure 3. These hydrogen bonds bring the moieties into a 2D network. When the 2D networks are packed along the a-axis, phen molecules from two adjacent 2D networks are parallel to each other; therefore a 3D supramolecular structure is formed by π–π stacking of phen molecules, as well as by hydrogen bonds, as shown in figure 4.

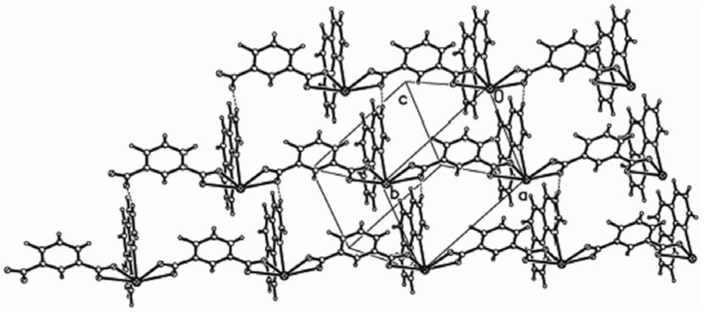

Figure 4. 3D network of **1**. Hydrogen bonds are shown in dotted line.

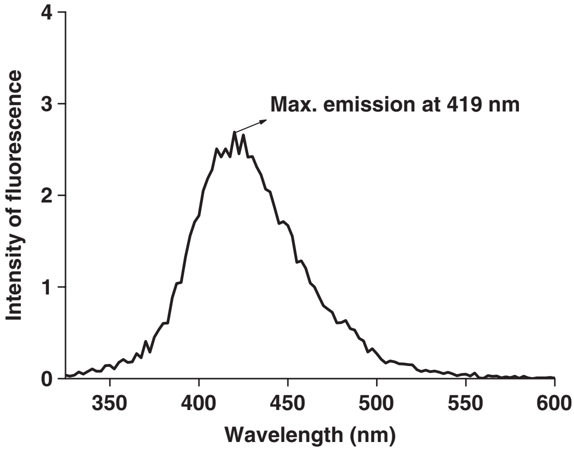

Figure 5. Fluorescence emission spectrum of **1** in the solid state at room temperature. λem(max) = 419 nm.

3.2. *Photophysical properties of (1)*

The electronic emission spectra of **1** in the solid state at room temperature are shown in figure 5. A salient feature of **1** is that it emits strong blue fluorescent light (λem(max) = 419 nm) when it is excited by UV lights (λex(max) = 310 nm). The emissions of the title compound can be assigned to π–π^* transition of 1,3-benzenecarboxylate ligand; a similar emission was observed for free ligand. The enhanced fluorescence of **1** probably arises from greater rigidity of the ligand coordinated to Pb^{2+} than the free ligand, which effectively reduces the loss of energy [14, 15]. The strong blue fluorescence indicates **1** may be a good candidate for blue-light photoactive materials.

Supplementary material

Crystallographic data for complex **1** is deposited to the Cambridge Crystallographic Data Center with deposition number CCDC 614010.

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