

Two new Pb coordination polymers derived from pyrimidine-2-thiolate: Synthesis, methyl substitution-induced effect and properties

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ARTICLE INFO

Article history:

Received 8 December 2015

Received in revised form

4 March 2016

Accepted 4 March 2016

Available online 9 March 2016

Keywords:

Coordination polymer

Substitution group

Pb

Crystal structure

ABSTRACT

Two new coordination compounds, $\{Pb(py\text{mt})_2\}_\infty$ (**1**) and $\{Pb(\text{mpy}\text{mt})_2\}_\infty$ (**2**) (pymt = pyrimidine-2-thiolate and mpymt = 4-methyl-pyrimidine-2-thione) have been synthesized under solvothermal conditions and characterized by elemental analyses, IR spectroscopy, thermogravimetric analysis, powder X-ray diffraction and single-crystal X-ray diffraction. In compounds **1** and **2**, pymt^- and mpymt^- adopt the same coordination modes ($\mu-1 \kappa\text{N}, \text{S}$ and $\mu_2-1 \kappa\text{N}, \text{S}: 2 \kappa\text{S}, \text{N}$) to interacted with Pb^{2+} , however, different topology structures for compounds **1** and **2** are obtained. Compound **1** displays a one-dimensional (1D) ribbon with square cavity constructed from two double concentric chains of $[\text{Pb-S}]_\infty$ and $[\text{Pb-Pyrimidine}]_\infty$ sharing Pb1 ions. Compound **2** shows 1D polymeric single chain constructed by $[\text{Pb-S}]_\infty$ and $[\text{Pb-methyl-pyrimidine}]_\infty$ chains. The results revealed that the methyl groups don't influence the coordination modes of pyrimidine-2-thiolate but directed the structural variations. Moreover, the fluorescent properties of compounds **1** and **2** were investigated.

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1. Introduction

Organic sulfur ligands as organic building blocks in coordination chemistry have attracted considerable interest owing to their versatile binding modes, good biological activities, excellent adsorbent properties for the retention of heavy metals and electronic properties [1–6]. Compared with the organic carboxylates, the coordination complexes based on organic sulfur ligands are more difficult to synthesize due to their rich redox chemistry based on both oxidative formation and reduction cleavage of the C–S bond [7–18].

Recently, pyrimidine-2-thiolate (pymt), which contains two heterocyclic nitrogen atoms adjacent to the thioamide group and show thione-thiol ($-\text{N}=\text{C}-\text{SH} \leftrightarrow -\text{NH}-\text{C}=\text{S}$) equilibrium, were widely applied to coordinate with transition, post-transition, and main group metal atoms in neutral and/or deprotonated ligands to assemble mono-, di-, tri-, tetra-, hexanuclear and polymeric complexes [19–34]. The analyses of the reported complexes based on pymt revealed that the research mainly focused on the synthesis of coordination compounds with metal centers Pd, Pt, Cu, Ag, Sn, Zn,

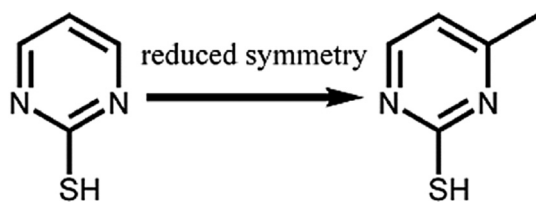
Cd, etc., however, the effect of substituent groups of pymt on the structure of the complexes are not reported yet. As the derivative of pymt, namely, 4-methyl-pyrimidine-2-thione (mpymt) is similar with pymt, however, the apparent differences between them are observed. On one hand, the methyl group of mpymt ligand may provide steric hindrance to influence the coordination modes and aggregation state of the final products; on the other hand, the introduction of methyl substituent groups lower the linker symmetry, which might induce the symmetry change of the target complexes (Scheme 1). So, the effects of substituent groups on the coordination modes of pyrimidine-2-thiolate as well as structures and properties of the targeted complexes were meaningful.

Following our interests on the preparation of coordination polymers based on organosulfur ligands [17], in this work, we have focused on the effect of substituent groups of pymt on the structure and function of the complexes. Pymt and mpymt are chosen as organic linkers to construct two new Pb coordination compounds, $\{Pb(py\text{mt})_2\}_\infty$ (**1**) and $\{Pb(\text{mpy}\text{mt})_2\}_\infty$ (**2**). Compound **1** displays a 1D ribbon with square cavity, different from the 1D polymeric single chain of compound **2**. We hope that the studies of the effects of the substituent units on the construction of the targeted complexes should contribute to deepen this research field.

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Scheme 1. The linker symmetry was reduced from pyymt to mpyymt.

2. Experimental section

2.1. Materials and measurements

All chemicals and solvents purchased were of reagent grade and were used without further purification. Elemental analysis (C, H, N) was performed on a Perkin–Elmer 240C elemental analyzer. Infrared (IR) spectra were obtained with KBr Pellets on a Perkin Elmer Spectrum One FT-IR spectrometer in the range 400–4000 cm^{-1} . Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGA-7000 thermogravimetric analyzer under the flowing nitrogen at a temperature ramp rate of 10 $^{\circ}\text{C min}^{-1}$. Powder X-ray diffraction (PXRD) patterns of the samples were recorded by a RIGAKU-DMAX2500 X-ray diffractometer with Cu K α radiation. Photoluminescence (PL) excitation and emission spectra were recorded with a Jobin Yvon Fluoro Max-4 spectrophotometer equipped with a 150 W xenon lamp as the excitation source at room temperature.

2.1.1. Synthesis of $\{Pb(pyymt)_2\}_{\infty}$ (**1**)

A solution of pyymt (5.6 mg, 0.05 mmol) in 6 mL water/methanol/DMF mixed solution (v:v = 3:2:1) was directly mixed with a 1 mL 0.10 mol L $^{-3}$ Pb(Ac) $_2 \cdot 3H_2O$ solution at room temperature in a 15 mL beaker. The resulted mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel reactor, and heated at 100 $^{\circ}\text{C}$ for 72 h. Upon cooling to room temperature, the colorless crystals were filtered and washed with ethanol. Yield: 65% (based on pyymt). Elemental anal. Calcd C $_8$ H $_6$ PbS $_2$ N $_4$ (429): C 22.38, H 1.40, N 13.05; Found: C 22.35, H 1.38, N 13.04. IR data (KBr, cm^{-1}): 2934(w), 1566(s), 1539(s), 1371(s), 1175(m), 745(m), 640(w).

2.1.2. Synthesis of $\{Pb(mpyymt)_2\}_{\infty}$ (**2**)

The procedure was the same as that for **1** except that pyymt was replaced by mpyymt (6.3 mg, 0.05 mmol). Upon cooling to room temperature, the yellow crystals were filtered and washed with ethanol. Yield: 47% (based on mpyymt). Elemental anal. Calcd. C $_{10}$ H $_{10}$ PbN $_4$ S $_2$ (457): C 26.26, H 2.19, N 12.25; Found: C 26.29, H 2.20, N 12.24%. IR data (KBr, cm^{-1}): 2924(w), 1576(s), 1545(s), 1371(m), 1170(m), 747(m), 642(m).

2.2. Crystal structure determination

The crystal structures were determined by single-crystal X-ray diffraction. Reflection data were collected on a Bruker SMART CCD area-detector diffractometer (Mo-K α radiation, graphite monochromator) at room temperature with ω -scan mode. Empirical adsorption corrections were applied to all data using SADABS. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL 97 software [35]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the ligands were localized in their calculated positions and refined using a riding model. The crystallographic data and pertinent information for compounds **1** and **2** are given in Table 1; selected bond lengths and angles in Table 2.

Table 1
Crystal data and structure refinement for compounds **1** and **2**.

Compounds	1	2
Empirical formula	C $_8$ H $_6$ N $_4$ PbS $_2$	C $_{10}$ H $_{10}$ N $_4$ PbS $_2$
Formula weight	429.51	457.53
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2 $_1$ /n
a, Å	27.479 (5)	8.0210 (16)
b, Å	8.5250 (17)	8.1097 (16)
c, Å	14.635 (3)	19.697 (4)
α , deg	90	90
β , deg	109.58 (3)	94.89 (3)
γ , deg	90	90
Volume (Å 3)	3230.1 (11)	1276.6 (4)
Z	12	4
$\rho_{\text{calc}}/\text{gcm}^{-3}$	2.650	2.381
Absorption coef./mm $^{-1}$	16.026	13.524
θ range ($^{\circ}$)	3.05–27.48	3.26–27.48
Crystal size (mm 3)	0.30 \times 0.28 \times 0.14	0.33 \times 0.12 \times 0.11
Reflections collected	15036	12155
Unique reflections (Rint)	3685 (0.1043)	2926 (0.0413)
Completeness	99.8%	99.7%
Goodness-of-fit on F^2	1.018	1.083
R indexes [$I > 2\sigma(I)$] ^a	R1 = 0.0401, wR2 = 0.0948	R1 = 0.0256, wR2 = 0.0522
R (all data) ^a	R1 = 0.0479, wR2 = 0.0988	R1 = 0.0327, wR2 = 0.0545

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

Table 2
Bond lengths (Å) and Angles (deg) for compounds **1** and **2**.

Compound 1			
Pb(1)–N (1)	2.656 (5)	N (3)–Pb(2)–N (2)	137.64 (15)
Pb(1)–S (1)	2.7922 (17)	N (3)–Pb(2)–S (3)#2	88.43 (12)
Pb(1)–N (5)	2.969 (5)	N (2)–Pb(2)–S (3)#2	85.78 (11)
Pb(1)–S (3)	3.3914 (18)	N (3)–Pb(2)–S (2)	58.69 (12)
Pb(2)–N (3)	2.583 (5)	N (2)–Pb(2)–S (2)	79.44 (11)
Pb(2)–N (2)	2.672 (5)	S (3)#2–Pb(2)–S (2)	90.80 (5)
Pb(2)–S (3)#2	2.7200 (17)	N (3)–Pb(2)–N (6)#2	75.82 (16)
Pb(2)–S (2)	2.7526 (17)	N (2)–Pb(2)–N (6)#2	131.24 (14)
Pb(2)–N (6)#2	2.907 (5)	S (3)#2–Pb(2)–N (6)#2	55.82 (10)
Pb(2)–S (1)	3.3295 (17)	S (2)–Pb(2)–N (6)#2	124.55 (12)
S (1)–C (1)	1.720 (6)	N (3)–Pb(2)–S (1)	170.20 (12)
S (2)–C (5)	1.729 (5)	N (2)–Pb(2)–S (1)	50.93 (11)
S (3)–C (9)	1.724 (6)	S (3)#2–Pb(2)–S (1)	87.67 (5)
N (1)#1–Pb(1)–N (1)	124.9 (2)	S (2)–Pb(2)–S (1)	130.33 (4)
N (1)#1–Pb(1)–S (1)#1	57.83 (11)	N (6)#2–Pb(2)–S (1)	94.58 (11)
N (1)–Pb(1)–S (1)#1	81.39 (12)	S (3)–Pb(1)–S (3)#1	92.98 (6)
N (1)–Pb(1)–S (1)	57.83 (11)	N (5)#1–Pb(1)–S (3)#1	48.52 (11)
S (1)#1–Pb(1)–S (1)	84.96 (8)	N (5)–Pb(1)–S (3)#1	101.62 (11)
N (1)#1–Pb(1)–N (5)	85.46 (15)	S (1)–Pb(1)–S (3)#1	168.18 (5)
N (1)–Pb(1)–N (5)	112.87 (15)	S (1)#1–Pb(1)–S (3)#1	92.11 (5)
S (1)#1–Pb(1)–N (5)	140.25 (11)	N (1)–Pb(1)–S (3)#1	133.08 (10)
S (1)–Pb(1)–N (5)	74.03 (11)	N (1)#1–Pb(1)–S (3)#1	87.34 (12)
N (1)#1–Pb(1)–N (5)#1	112.87 (15)	N (5)#1–Pb(1)–S (3)	101.62 (11)
N (1)–Pb(1)–N (5)#1	85.46 (15)	N (5)–Pb(1)–S (3)	48.52 (11)
S (1)#1–Pb(1)–N (5)#1	74.03 (11)	S (1)–Pb(1)–S (3)	92.11 (5)
S (1)–Pb(1)–N (5)#1	140.25 (11)	S (1)#1–Pb(1)–S (3)	168.18 (5)
N (5)–Pb(1)–N (5)#1	140.9 (2)	N (1)–Pb(1)–S (3)	87.34 (12)
N (1)#1–Pb(1)–S (3)	133.08 (10)		
Compound 2			
N (2)–Pb(1)#3	2.673 (4)	N (3)–Pb(1)–S (1)	90.54 (8)
N (3)–Pb(1)	2.653 (4)	N (2)#4–Pb(1)–S (1)	87.28 (8)
N (1)–Pb(1)	2.884 (4)	S (2)–Pb(1)–S (1)	89.76 (4)
Pb(1)–S (2)	2.7065 (15)	S (1)–Pb(1)–S (1)#4	86.24 (3)
Pb(1)–S (1)	2.7081 (12)	N (1)–Pb(1)–S (1)#4	82.711 (7)
Pb(1)–S (1)#4	3.4755 (14)	N (2)#2–Pb(1)–S (1)#4	48.984 (8)
N (3)–Pb(1)–N (2)#4	139.55 (13)	S (2)–Pb(1)–S (1)#2	129.70 (3)
N (3)–Pb(1)–S (2)	58.83 (10)	N (3)#4–Pb(1)–S (1)#2	170.76 (1)
N (2)#4–Pb(1)–S (2)	80.77 (9)	N (2)#4–Pb(1)–N (1)	122.67 (10)
N (3)–Pb(1)–N (1)	88.31 (11)	S (1)–Pb(1)–N (1)	56.50 (8)
S (2)–Pb(1)–N (1)	133.83 (8)		

Symmetry codes: #1 $-x, y, -z-1/2$; #2 $x, y+1, z$; #3 $-x+1/2, y-1/2, -z+3/2$; #4 $-x+1/2, y+1/2, -z+3/2$.

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