

LEAD(II) COORDINATION POLYMERS DERIVED FROM SIMPLE HETEROAROMATIC CARBOXYLIC ACIDS: STRUCTURAL, THERMAL AND LUMINESCENCE STUDIES



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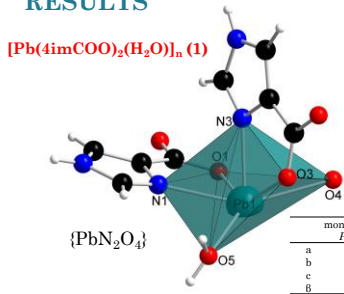
INTRODUCTION

The design and construction of metal coordination polymers (MCPs) is one of the most active areas of materials research. The intense interest in this field is driven by both their interesting network topologies and potential applications such as catalysis, sensors, molecular magnets, drug delivery, adsorption, ion exchange and luminescence materials. Recently, many efforts had been made in the studies of MCPs, devoted to d- and f-block metal ions complexes. As an important p-block element, Pb(II) may provide opportunities for the formation of novel topological arrangements with photochemical and photophysical properties [1]. This is due to the large ionic radius, the presence of inert electron pair and flexible coordination environment. On the other hand, heteroaromatic carboxylic acids exhibit multiple coordinating modes facilitating the formation of multi-dimensional structures and diversified topologies [2].

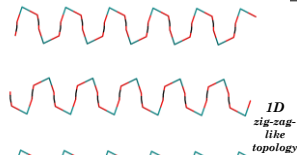
Herein, we report the solid-state studies of three novel lead(II) coordination polymers derived from imidazole-4-carboxylic acid (4imCOOH), pyrazole-3-carboxylic acid (3pyrCOOH), and thiophene-3-carboxylic acid (3tpCOOH). Complex (1), namely $[Pb(4imCOO)_2(H_2O)]_n$, is 1D polymer, whereas complexes (2) and (3), namely $[Pb(3pyrCOO)_2]_n$ and $[Pb(3tpCOO)_2(\mu-H_2O)]_n$, respectively, are 2D polymers. Their structures can be extended into 3D supramolecular frameworks by weak interactions. All three compounds exhibit interesting fluorescence properties in the solid state, especially compound (2) with double fluorescence. Moreover compounds have been characterized by elemental (CHNS), spectral (FT-IR) and thermal (TGA) analysis.

RESULTS

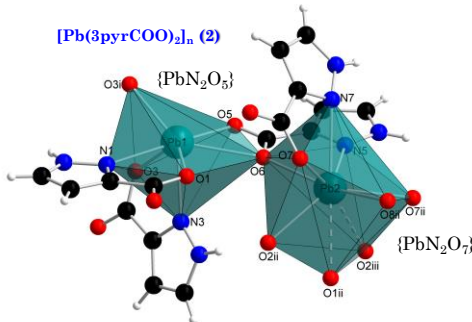
[Pb(4imCOO)₂(H₂O)]_n (1)



monoclinic <i>P2₁/c</i>	
a	7.31759 Å
b	22.723 Å
c	6.9519 Å
β	109.13°



[Pb(3pyrCOO)₂]_n (2)



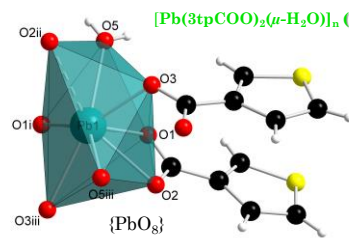
monoclinic <i>P2₁/c</i>	
a	11.0302 Å
b	23.6286 Å
c	8.6039 Å
β	110.274°

2D basket weave-like topology

Coordination bonds distances for (2) [Å]

Pb1-O3	2.445	Pb2-O7	2.523
Pb1-N3	2.487	Pb2-O7 ⁱⁱ	2.583
Pb1-N1	2.623	Pb2-O6	2.634
Pb1-O5	2.642	Pb2-O8 ⁱⁱ	2.670
Pb1-O3 ⁱⁱ	2.692	Pb2-O2 ⁱⁱ	2.724
Pb1-O1	2.694	Pb2-N5	2.739
Pb1-O6	2.717	Pb2-N7	2.776
		Pb2-O1 ⁱⁱ	2.893
		Pb2-O2 ⁱⁱ	3.156

[Pb(3tpCOO)₂(μ -H₂O)]_n (3)



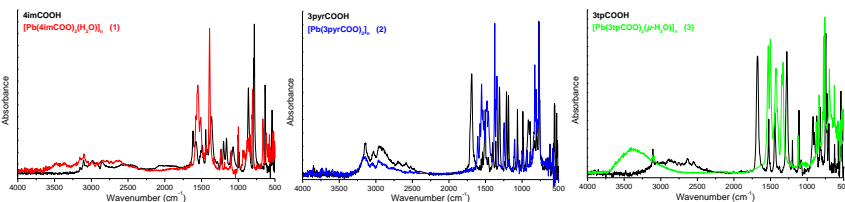
monoclinic <i>P2₁/c</i>	
a	15.392 Å
b	7.5978 Å
c	11.104 Å
β	105.67°

2D honeycomb-like topology

Coordination bonds distances for (3) [Å]

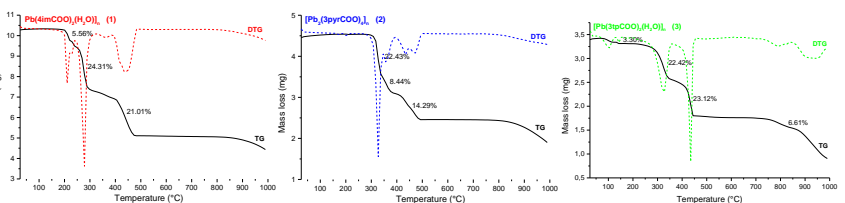
Pb1-O3	2.470	Pb1-O3 ⁱⁱ	2.646
Pb1-O1	2.506	Pb1-O5 ⁱⁱ	2.749
Pb1-O2	2.541	Pb1-O1 ⁱⁱ	2.736
Pb1-O5	2.626	Pb1-O2 ⁱⁱ	2.995

Coordination bonds distances for (1) [Å]			
Pb1-N3	2.420	Pb1-O3	2.594
Pb1-N1	2.453	Pb1-O4	2.737
Pb1-O1	2.455	Pb1-O5	2.775



FT-IR spectra of complexes 1, 2, 3 and starting ligands

	The characteristic IR bands of ligands and reported complexes [cm ⁻¹]				
	$\nu(O-H)_2$	$\nu(O-H)COOH$	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\nu(\text{ring})$
4imCOOH	2600-2350	-	-	-	1616, 1576, 1508, 1489
(1)	3600-3200	-	1558, 1546	1387	1572, 1507, 1436
3pyrCOOH	2800-2400	1688	-	-	1558, 1541, 1504, 1464
(2)	-	-	1550, 1533, 1515	1370, 1351, 1340	1574, 1492, 1476, 1456
3tpCOOH	3200-2400	1677	-	-	1524, 1442
(3)	3700-2900	-	1528	1339, 1325	1500, 1424, 1415

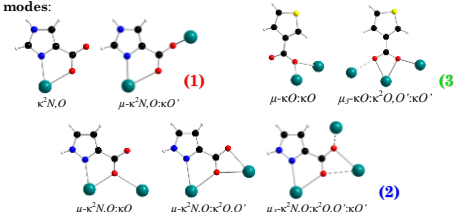


TG/DTG curves of complexes 1, 2 and 3

CONCLUSIONS

1. All three obtained complexes are coordination polymers: (1) is 1D polymer with zig-zag-like topology (CN=6); (2) is 2D polymer with basket weave-like topology (two Pb centers with CN=7 and 9); and (3) is 2D polymer with honeycomb-like topology (CN=8).

2. The carboxylate anions act in complexes in different coordination modes:



- Structural data indicate hemidirected type of coordination around Pb(II) ions, with stereochemically active lone pair.
- The Δ values, defined by Deacon and Phillips [3], are very well consistent with X-ray diffraction measurements.
- The complexes are thermally stable to temperature: (1) 200°C, (2) 300°C, and (3) 75°C, and pure metals were final solid products of thermal decomposes.
- Compared with the ligands, the photoluminescence properties of (1) and (3) are much more enhanced, while fluorescence intensity of (2) is lower. Higher energy emission bands can be attributed to the ligand-to-metal charge transfer (LMCT) as a consequence in the intraligand $n-\pi^*$ and/or $n-\pi^*$ transitions. Additional low energy emission maxima around 550 nm in spectra of (2) and (3), with large Stokes shift, can be assigned to the metal-centered (MC) transitions involving s^2 lone pair and empty p orbitals.

References

- S.-J. Zhan, Y. Sun, S.-P. Li, G.-M. Tang, Y.-T. Wang, Y.-Z. Cui, *Polyhedron* 121 (2017) 252.
- M.-L. Hu, A. Morsali, I. Aboutorabi, *Coord. Chem. Rev.* 255 (2011) 2821.
- G.B. Deacon, R.J. Phillips, *Coord. Chem. Rev.* 33 (1980) 227.

Solid-state 3D fluorescence spectra of ligands (top) and complexes 1, 2 and 3 (down)

