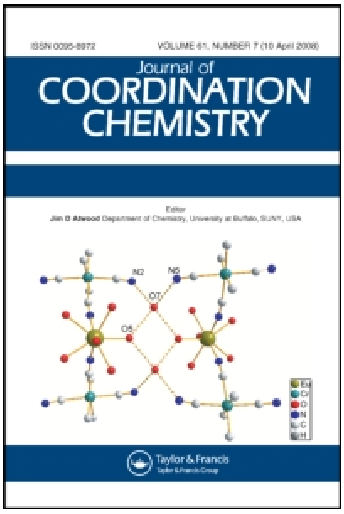

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Thermal, spectroscopic, X-ray powder diffraction, fluorescence, and structural studies of [Pb(μ-4-pyc)(μ-Br)]<i>_n, new mixed-anion lead(II) 3-D coordination polymers

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To cite this Article Ramazani, Ali , Dolatyari, Leila , Morsali, Ali and Kassaee, Mohammad Zaman(2009) 'Thermal, spectroscopic, X-ray powder diffraction, fluorescence, and structural studies of [Pb(μ-4-pyc)(μ-Br)]**<i>_n**, new mixed-anion lead(II) 3-D coordination polymers', Journal of Coordination Chemistry, 62: 11, 1784 — 1790

To link to this Article: DOI: 10.1080/00958970902721543

URL: http://dx.doi.org/10.1080/00958970902721543

Journal of Coordination Chemistry
Vol. 62, No. 11, 1 June 2009, 1784–1790

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Thermal, spectroscopic, X-ray powder diffraction, fluorescence, and structural studies of [Pb(μ-4-pyc)(μ-Br)]$_n$, new mixed-anion lead(II) 3-D coordination polymers

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(*Received 3 May 2008; in final form 10 September 2008*)

A new Pb(II) 3-D coordination polymer, [Pb(μ-4-pyc)(μ-Br)]$_n$ (**1**) {4-Hpyc = 4-pyridinecarboxylic acid}, has been synthesized and characterized by elemental analysis, IR spectroscopy, and structure determined by single-crystal X-ray diffraction. The crystal structure consists of 3-D polymeric units. The thermal stability of **1** was studied by thermal gravimetric and differential thermal analyses.

Keywords: Lead(II); Crystal structure; Mixed-anion complex; 4-Pyridinecarboxylic acid; Thermal stability

1. Introduction

Interest has focused on new discrete supramolecular complexes and coordination polymers based on polydentate organic ligands due to their novel structural topologies and potential applications in sensing, catalysis, ion exchange, separations, or gas storage. Various intriguing molecular frameworks have been designed and synthesized by direct combination of the basic components. Coordination geometry of metal cations, the binding site of donating atoms, and the length and shape of spacers by the induction of weak intra- and/or inter-molecular interactions are important [1–6]. Metal organic frameworks (MOFs) of Pb(II) [7] have rich structures and diverse coordination geometries. Pb(II) has a 6s lone pair of electrons which affects the coordination geometry. The stereochemical active 6s electrons usually produce hemidirected geometry for they can take up more space and leave a distinct void or gap in the coordination sphere ([8, 9], for a review on the coordination chemistry of lead(II) see [10]); when the 6s electrons of Pb(II) are stereochemically inactive the void or gap disappears [9], resulting in the holodirected coordination geometry. The bonding limit

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902721543

can determine the coordination geometry of Pb(II) to a certain extent. With potential ligands, farther from Pb(II) due to repulsion of the 6s electrons, the hemidirected coordination sphere changes to holodirected [11–13]. In this article, we have synthesized and characterized a new hemidirected lead complex [Pb(μ-4-pyc)(μ-Br)]$_n$ (**1**) {4-Hpyc = 4-pyridinecarboxylic acid}, with interesting 3-D structure and stereochemically active 6s electrons.

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. X-ray powder diffraction (PXRD) measurements were performed using a Philips diffractometer manufactured by X'pert with monochromated Cu-Kα radiation; simulated X-ray diffraction (XRD) powder patterns based on single crystal data were prepared using Mercury [14a, 15a]. The thermal behavior was measured with PL-STA 1500 apparatus. Crystallographic measurements were made at 100(2) K using a Bruker AXS SMART APEX CCD diffractometer. The intensity data were collected using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. Molecular structure plots were prepared using Mercury [14a] and ORTEPIII [14b].

2.2. *Preparation of [Pb(μ-4-pyc)(μ-Br)]$_n$ (1)*

For preparation of **1**, we used the branched tube method [15–17]. 4-Hpyc (0.123 g, 1 mmol), lead(II) nitrate (0.331 g, 1 mmol), and potassium bromide (0.119 g, 1 mmol) were placed in the arm to be heated. Methanol was carefully added to fill both arms, then the arm to be heated was placed in a bath at 60°C. After 10 days, brown crystals deposited in the cooler arm were filtered off, washed with acetone and methanol and air dried. Yield 45%; m.p. = 98°C. Anal. Calcd for $C_6H_4BrNO_2Pb$ (%): C, 17.58; H, 0.97; N, 3.42. Found: C, 17.35; H, 1.10; N, 3.60. IR (selected bands; in cm^{-1}): 603 m, 701 s, 833 m, 924 w, 120 rm, 1414 s, 1444 m, 1525 vs, 1559 m, 3020 w.

3. Results and discussion

Reaction between 4-Hpyc, lead(II) nitrate, and potassium bromide by diffusion along a thermal gradient in a methanolic solution (the branched tube method) produced [Pb(μ-4-pyc)(μ-Br)]$_n$ (**1**) as brown crystals. The compound is air-stable and soluble in DMSO.

The IR spectrum of **1** shows characteristic absorption bands for 4-pyc$^-$ with variable intensity in the frequency range 1400–1580 cm^{-1} from ring vibrations of the py moiety of 4-pyc$^-$, and symmetric and asymmetric vibrations of the carboxylate at

Table 1. Crystal data and structure refinement for $[Pb(\mu\text{-4-pyc})(\mu\text{-Br})]_n$.

Identification code	$[Pb(\mu\text{-4-nic})(\mu\text{-Br})]_n$
Empirical formula	$C_6H_4BrNO_2Pb$
Formula weight	409.20
Temperature (K)	100(2)
Wavelength	0.71073
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	11.695(4)
b	17.175(6)
c	7.861(3)
β	91.037(7)
Volume (Å^3)	1578.7(9)
Z	8
Density (Calcd) (mg m^{-3})	3.443
Absorption coefficient	26.379
F (000)	1440
Crystal size (mm^3)	0.11 × 0.10 × 0.04
θ range for data collection (°)	2.11 to 28.28
Index ranges	$-15 \leq h \leq 14$ $-22 \leq k \leq 2$ $-10 \leq l \leq 10$
Reflections collected	63368
Independent reflections	1932 (R(int) = 0.0748)
Absorption correction	Multi-scan
Maximum and minimum transmission	0.348 and 0.048
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1932/74/100
Goodness-of-fit on F^2	1.103
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0972$ and $wR_2 = 0.2662$
R Indices (all data)	$R_1 = 0.1169$ and $wR_2 = 0.2907$
Largest difference peak, hole (e Å^{-3})	10.377 and −7.399

1414 and 1559 cm^{-1}. The $\Delta(\nu_{asym} - \nu_{sym})$ value of 145 cm^{-1} indicates that carboxylate groups bridge lead(II) centers [18].

Determination of the structure of $[Pb(\mu\text{-4-pyc})(\mu\text{-Br})]_n$ (**1**) by X-ray crystallography (tables 1 and 2) show the complex to be a 3-D polymeric network in the solid state (figures 1 and 2). The structure may be considered as a coordination polymer of lead(II) consisting of 1-D linear chains, running parallel to the *c*-axis, with a building block of $[PbBr_2]$. Br^- doubly bridges two lead(II) ions. The intra-chain Pb···Pb distance within the $[PbBr_2]_n$ chains is 4.349 Å, while those bridged by 4-nic$^-$ are 8.554 and 9.783 Å. The individual polymeric chains are almost parallel and further bridged by bidentate 4-nic$^-$, resulting in a 3-D framework as shown in figure 2(b).

Coordination around lead is hemidirected with arrangement of 4-pyc$^-$ and bromide suggesting a gap or hole in coordination geometry around the metal [$O1^{iii}$–Pb1–Br1 and $O2^{iii}$–Pb1–$Br1^{i}$ with the angles 164.5(3) and 165.2(2)°, respectively], indicating that the lone pair of electrons on lead(II) is sterically active. There are three different Pb–O bond lengths in the Pb coordination sphere of **1**, Pb1–$O1^{ii}$ = 2.669(16), Pb1–$O2^{iii}$ = 2.392(14), and Pb1–$O1^{iii}$ = 3.095(14) Å. These Pb–O distances are in the range commonly observed [19] and can be considered bonding interactions. The observed shortening of the Pb–O

Table 2. Bond lengths (Å) and angles (°) for $[Pb(\mu\text{-4-pyc})(\mu\text{-Br})]_n$.

Pb1–Br1	2.867(3)
Pb1–Br1^{i}	3.176(2)
Pb1–N1	2.451(19)
Pb1–O1^{ii}	2.669(16)
Pb1–O2^{iii}	2.392(14)
Pb1–O1^{iii}	3.095(14)
O2^{iii}–Pb1–N1	79.6(6)
O2^{iii}–Pb1–O1^{ii}	82.6(5)
N1–Pb1–O^{ii}	81.8(6)
O2^{iii}–Pb1–Br1	89.6(4)
N1–Pb1–Br1	83.7(5)
O1^{ii}–Pb1–Br1	164.5(3)
N1–Pb1–Br1^{i}	85.8(5)

i: $x, -y+1, z-1/2$; ii: $-x+3/2, -y+1/2, -z+1$; iii: $x+1/2, -y+1/2, z-1/2$.

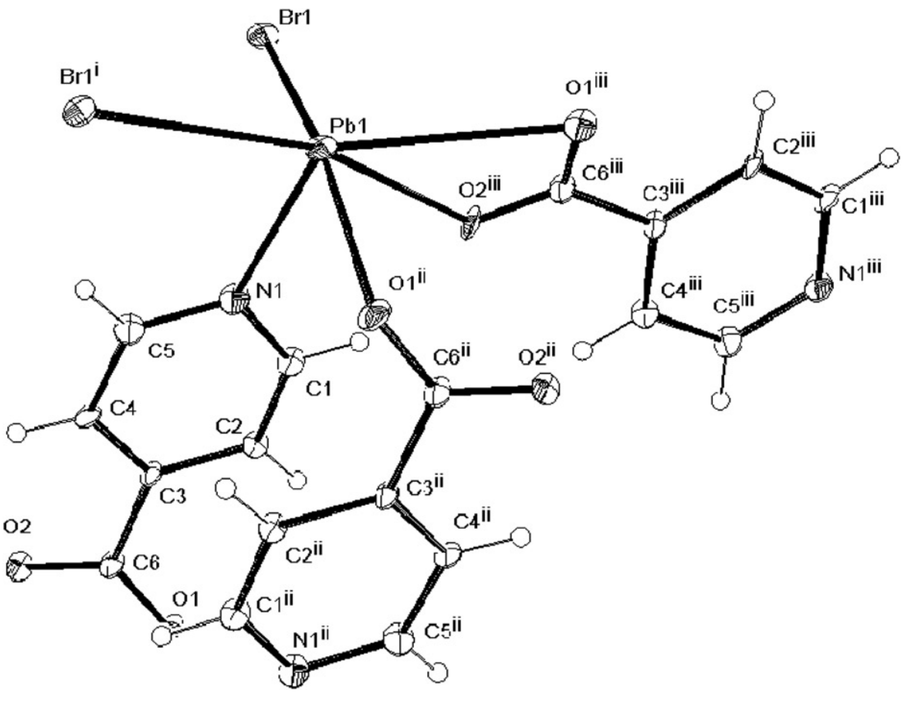

Figure 1. An ORTEP diagram showing coordination environment of Pb in $[Pb(\mu\text{-4-pyc})(\mu\text{-Br})]_n$. i: $x, -y+1, z-1/2$; ii: $-x+3/2, -y+1/2, -z+1$; iii: $x+1/2, -y+1/2, z-1/2$.

bond on the side of Pb(II) opposite to the putative lone pair 2.392(14) Å compared with 3.095(14) Å adjacent to the lone pair in this compound supports the presence of a sterically active lone pair [20].

There are π–π stacking [21, 22] interactions between parallel aromatic rings of adjacent chains as shown in figure 3. Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the π-stacking type, rather than

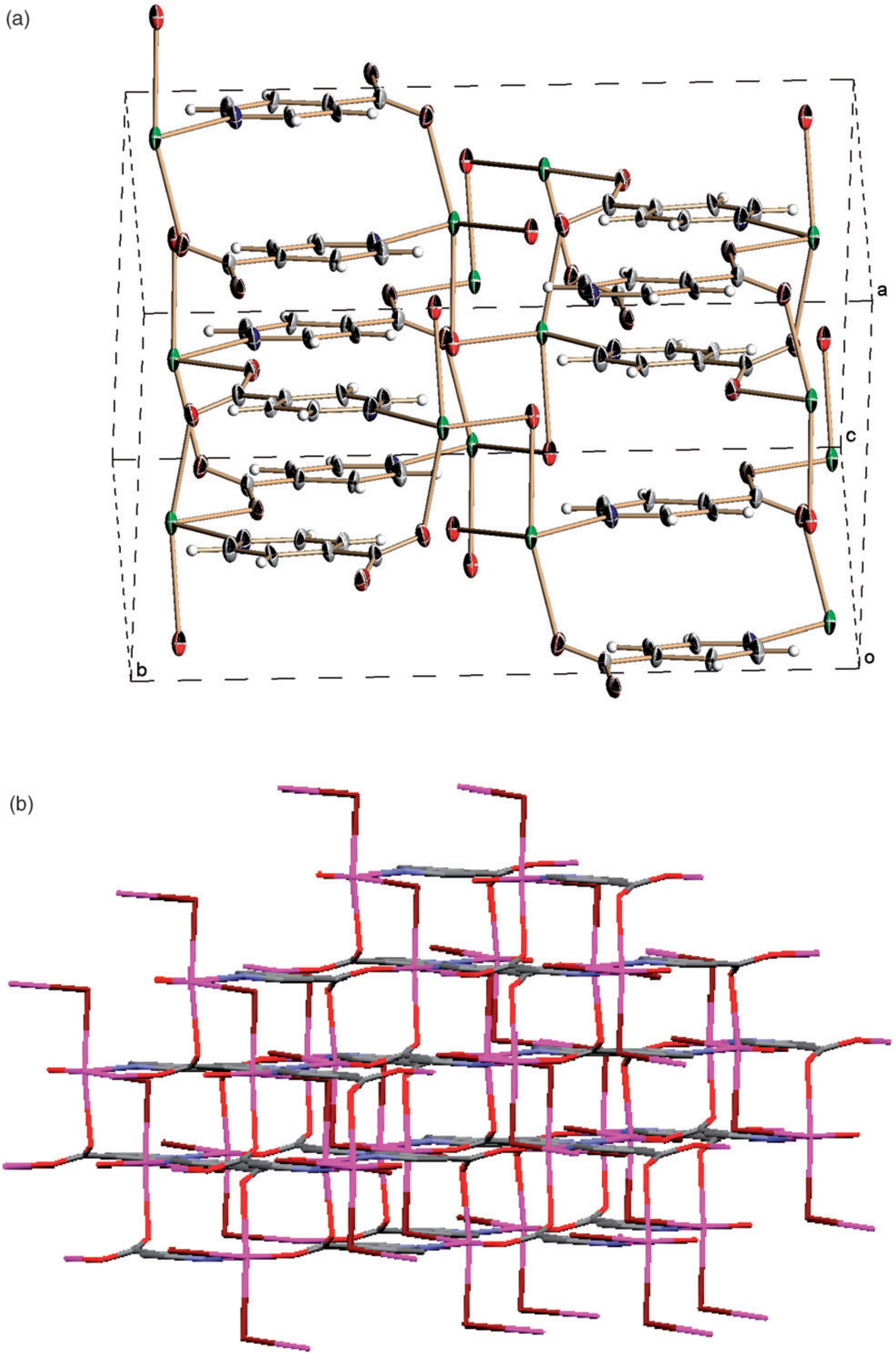

Figure 2. (a) Unit cell and (b) 3-D coordination polymer in $[Pb(\mu\text{-4-pyc})(\mu\text{-Br})]_n$.

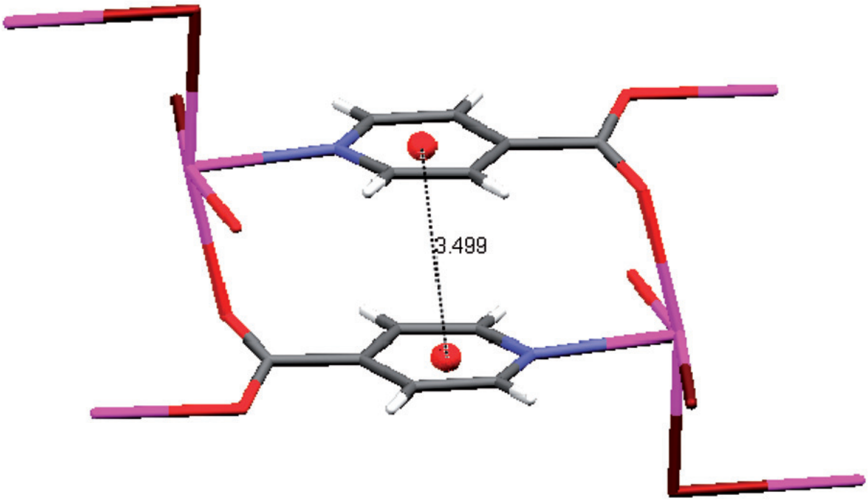

Figure 3. π–π stacking in $[Pb(\mu\text{-}4\text{-pyc})(\mu\text{-Br})]_n$.

"edge-to-face" or "vertex-to-face" types ([22], [23 and references therein]). In the structure reported here, the interplanar distance is *ca* 3.50 Å, normal for π–π stacking ([23 and references therein], [24]). Thus two factors, lone pair activity and π–π stacking control the coordination sphere of this complex. The obvious question then is whether the lone pair activity has stretched coordinate bonds to result in ligand stacking or whether it is the stacking interaction, which has imposed a positioning of the donor atoms for forming a gap in the coordination sphere.

The thermal stability of **1** has been determined on a single crystal sample between 0 and 700°C in air by thermogravimetric (TG) and differential thermal analyses (DTA) (Supplementary material). TGA shows that decomposition starts at about 275°C and ends at 400°C with 44.50% weight loss; the remaining weight corresponds to PbO. The XRD pattern is in agreement with the cubic PbO diffraction. The DTA curve displays a distinct endothermic peak at 90°C as well as three exothermic peaks at 275, 345, and 390°C.

Solid $[Pb(\mu\text{-}4\text{-pyc})(\mu\text{-Br})]_n$ (**1**) show very similar photoluminescent spectra of ligand 4-Hpyc. Compound **1** exhibits four fluorescence emission maxima at 430, 485, 520, and 535 nm upon photoexcitation at 370 nm. These emission peaks are virtually the same as for 4-Hpyc, 432, 485, 520, and 535 nm, indicating that they are not influenced by coordination of the 4-Hpyc or by the structural geometry.

The isolated samples of $[Pb(\mu\text{-}4\text{-pyc})(\mu\text{-Br})]_n$ (**1**) were also characterized by PXRD at room temperature. The experimental pattern for **1** is in good agreement with the calculated diffractograms (Supplementary material), thus pointing to the formation of only a single phase product under the reaction conditions.

Supplementary material

Crystallographic data for the structures reported in this article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication

No. CCDC-686654. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44–1223/336033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgment

This work was supported by the Islamic Azad University-Zanjan Branch and Tarbiat Modares University.

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