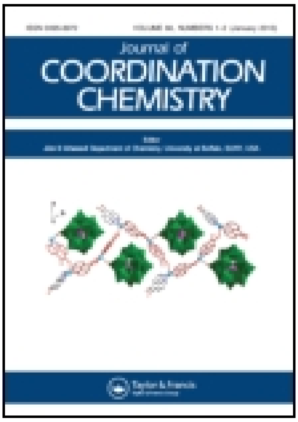

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

The first crystal structures of two 2-D lead(II)-coordination polymers with picolinic acid N-oxide and pseudohalides extended to 3-D networks by intermolecular interactions

Farzin Marandi [a] , Ching Kheng Quah [b] & Hoong-Kun Fun [b c]
[a] Department of Chemistry , Payame Noor University , Tehran , Islamic Republic of Iran
[b] X-ray Crystallography Unit , School of Physics, Universiti Sains Malaysia , Penang , Malaysia
[c] Department of Pharmaceutical Chemistry , College of Pharmacy, King Saud University , Riyadh , Saudi Arabia

To cite this article: Farzin Marandi , Ching Kheng Quah & Hoong-Kun Fun (2013) The first crystal structures of two 2-D lead(II)-coordination polymers with picolinic acid N-oxide and pseudohalides extended to 3-D networks by intermolecular interactions, Journal of Coordination Chemistry, 66:6, 986-994, DOI: 10.1080/00958972.2013.772145

To link to this article: http://dx.doi.org/10.1080/00958972.2013.772145

Journal of Coordination Chemistry
Vol. 66, No. 6, 20 March 2013, 986–994

The first crystal structures of two 2-D lead(II)-coordination polymers with picolinic acid *N*-oxide and pseudohalides extended to 3-D networks by intermolecular interactions

FARZIN MARANDI*†, CHING KHENG QUAH‡ and HOONG-KUN FUN‡§

†Department of Chemistry, Payame Noor University, Tehran, Islamic Republic of Iran
‡X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, Penang, Malaysia
§Department of Pharmaceutical Chemistry, College of Pharmacy, King Saud University, Riyadh, Saudi Arabia

(*Received 27 June 2012; in final form 5 November 2012*)

Two-dimensional lead(II)-azido and -thiocyanato coordination polymers with picolinate *N*-oxide (PNO), $[Pb(PNO)(NCS)]_n$ (**1**) and $[Pb(PNO)(N_3)]_n$ (**2**) were synthesized and characterized by elemental and thermal analyses, IR and ^1H NMR spectroscopy, and X-ray crystallography. Compound **1** crystallized in the chiral space group $P2_12_12_1$, whereas **2** adopts the centrosymmetric $P2_1/c$ space group. Multiple weak C–H···O and C–H···N interactions assemble the polymeric layers into 3-D supramolecular networks.

Keywords: Coordination polymers; Picolinic acid *N*-oxide; Lead(II)

1. Introduction

A goal of materials chemistry is to synthesize crystalline metal–organic frameworks. As multifunctional nitrogen and oxygen donors, pyridine carboxylic acid and pyridine carboxylic acid *N*-oxide ligands have been extensively employed in preparation of coordination polymers [1]. However, compounds containing picolinic acid *N*-oxide (HPNO) with pseudohalides received less attention in coordination chemistry [2]. Picolinic acid *N*-oxide (PNO) was chosen based on several considerations: (i) the carboxylato group in PNO may bind to metal ions with various coordination modes to form monomeric and polymeric compounds [3–5]; (ii) the carboxylato group may coexist with azide to bridge adjacent metal centers, giving mixed-bridged complexes; (iii) both the carboxylato and the *N*-oxide groups of PNO have ability to coordinate, which make PNO a good linker to incorporate metal-azido and -thiocyanato skeletons into coordination networks of high dimensionality; and (iv) the different coordination geometries exhibited by PNO may have significant influence on the structures of the frameworks, as observed in our previous work [6]. To understand the coordination chemistry of pyridine carboxylic acid *N*-oxide and prepare materials with good physical properties, we have engaged in research of coordination

---

*Corresponding author. Email: f.marandi@gmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2013.772145

compounds based on isonicotinic acid *N*-oxide [7]. In this paper, $[Pb(PNO)(NCS)]_n$ (**1**) and $[Pb(PNO)(N_3)]_n$ (**2**) are reported.

2. Experimental

2.1. *Materials and measurements*

All chemicals were reagent grade and used without purification. FTIR spectra were collected on a Mattson 1000 spectrophotometer using KBr pellets from 450 to 4000 cm^{-1}. Elemental analyses (CHN) were performed using a Carlo ERBA model EA 1108 analyzer whereas ^1H NMR spectra were obtained using a Bruker spectrometer at 250 MHz in [D6]dimethyl sulfoxide (DMSO). Thermogravimetric analyses (TGA) were performed in N_2 with a flow rate of 20 ml min^{-1} on a Seiko Instruments thermal analyzer from 20 to 800 °C, with a heating rate of 10 °C/min in ceramic crucibles.

2.2. *Crystallography*

Diffraction data for **1** and **2** were collected at room temperature and 100 K (with an Oxford Cyrosystem Cobra low-temperature attachment), respectively. The data were collected using a Bruker SMART APEXII CCD diffractometer with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at a detector distance of 5 cm using APEXII software [8]. The collected data were reduced using SAINT [8] and empirical absorption corrections

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

	1	**2**
Identification code	$[Pb(PNO)(NCS)]_n$	$[Pb(PNO)(N_3)]_n$
Empirical formula	$C_7H_4N_2O_3PbS$	$C_6H_4N_4O_3Pb$
Formula weight	403.37	387.32
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions	$a = 5.5868(7)$ Å	$a = 11.0574(3)$ Å
	$b = 8.7166(11)$ Å	$b = 6.4069(2)$ Å
	$c = 18.668(2)$ Å	$c = 12.8321(3)$ Å
	$\alpha = 90.00°$	$\alpha = 90.00°$
	$\beta = 90.00°$	$\beta = 116.355(2)°$
	$\gamma = 90.00°$	$\gamma = 90.00°$
Volume	909.1(2) Å^3	814.58(4) Å^3
Z	4	4
Density (calculated)	2.947 g cm^{-3}	3.158 g cm^{-3}
Absorption coefficient	18.767 mm^{-1}	20.696 mm^{-1}
F(000)	728	696
θ range for data collection	2.58–32.65°	2.06–31.49°
Index ranges	$-8 \leq h \leq 8$	$-16 \leq h \leq 16$
	$-10 \leq k \leq 13$	$-9 \leq k \leq 9$
	$-21 \leq l \leq 28$	$-18 \leq l \leq 17$
Reflections collected	6574	10,136
Independent reflections	3122[R(int) = 0.0475]	2705[R(int) = 0.0529]
Completeness to theta	99.8%	99.9%
Data/restraints/parameters	3122/0/127	2705/0/127
Goodness-of-fit on F^2	1.028	1.113
Final R [$I_0 > 2\sigma(I_0)$]	$R1 = 0.0648$, $wR2 = 0.1778$	$R1 = 0.0557$, $wR2 = 0.1412$
R indices (all data)	$R1 = 0.0726$, $wR2 = 0.1868$	$R1 = 0.0573$, $wR2 = 0.1432$
Largest diff. peak, hole	7.35, −2.48 e.Å^{-3}	5.65, −3.13 e.Å^{-3}

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

1		**2**	
Pb1–O3	2.364(8)	Pb1–O1	2.387(5)
Pb1–O2	2.489(8)	Pb1–O2	2.563(6)
Pb1–O2$^{\mathrm{iv}}$	2.546(8)	Pb1–O2$^{\mathrm{ii}}$	2.586(5)
Pb1–N2	2.588(11)	Pb1–N2$^{\mathrm{i}}$	2.604(6)
Pb1–O3$^{\mathrm{ii}}$	2.744(9)	Pb1–N2	2.620(6)
Pb1···S1$^{\mathrm{iii}}$	3.042(4)	Pb1–O1$^{\mathrm{ii}}$	2.839(5)
Pb1···O1$^{\mathrm{iv}}$	3.138(9)	Pb1–O3$^{\mathrm{iii}}$	2.937(4)
Pb1···S1$^{\mathrm{i}}$	3.678(8)	Pb1–N4	2.996(4)
O3–Pb1–O2	67.2(3)	O1–Pb1–O2	68.67(17)
N2–Pb1–S1$^{\mathrm{i}}$	84.1(3)	O1–Pb1–O2$^{\mathrm{iii}}$	65.65(15)
O2–Pb1–O2$^{\mathrm{ii}}$	98.68(17)	O2–Pb1–O2$^{\mathrm{iii}}$	107.36(8)
O3–Pb1–N2	78.1(4)	O1–Pb1–N2$^{\mathrm{i}}$	82.50(18)
O2–Pb1–N2	78.5(3)	O2–Pb1–N2$^{\mathrm{i}}$	79.69(17)
O2$^{\mathrm{ii}}$–Pb1–N2	140.8(3)	O2$^{\mathrm{iii}}$–Pb1–N2$^{\mathrm{i}}$	140.64(18)
O3–Pb1–O3$^{\mathrm{iii}}$	101.70(2)	O1–Pb1–N2	80.41(18)
O3$^{\mathrm{iii}}$–Pb1–S1$^{\mathrm{i}}$	141.34(2)	O2–Pb1–N2	136.59(18)
O2$^{\mathrm{ii}}$–Pb1–O3$^{\mathrm{iii}}$	69.7(3)	O2$^{\mathrm{iii}}$–Pb1–N2	85.28(18)
N2–Pb1–O3$^{\mathrm{iii}}$	134.5(3)	N2–Pb1–N2$^{\mathrm{i}}$	66.3(2)
O3–Pb1–S1$^{\mathrm{i}}$	81.2(2)		
O2–Pb1–S1$^{\mathrm{i}}$	146.34(19)		
O2$^{\mathrm{ii}}$–Pb1–S1$^{\mathrm{i}}$	77.1(2)		

i: $0.5+x, -0.5-y, -z$
ii: $0.5+x, 0.5-y, -z$
iii: $-0.5+x, 0.5-y, -z$
iv: $-0.5+x, -0.5-y, -z$

i: $-1-x, -1-y, -1-z$
ii: $x, 1+y, +z$
iii: $-1-x, 0.5+y, -1.5-z$

were performed using SADABS [8]. The structures were solved using direct methods and refined using the least-squares method from Shelxtl [9]. All non-hydrogen atoms were refined anistropically and hydrogens were located and included at calculated positions. Materials for publication were prepared using Shelxtl [9] and OrtepIII [10]. Full crystallographic data, in CIF format, may be obtained from the Cambridge Crystallographic Data Center (CCDC-871085 for 1 and CCDC-871084 for 2) via www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi. The crystal data and structure refinement of **1** and **2** are summarized in table 1. Selected bond lengths and angles of **1** and **2** are listed in table 2.

2.3. *Synthesis of [Pb(PNO)(NCS)]$_n$ (1)*

PNO (0.104 g, 0.75 mmol) was placed in one arm of a branched tube [11] whereas lead(II) acetate (0.284 g, 0.75 mmol) and potassium thiocyanate (0.074 g, 0.75 mmol) were placed in the other arm. Methanol and water in a ratio of 1 : 2 were carefully added to fill both arms. The tube was then sealed and the ligand-containing arm was immersed in a bath at 60 °C whereas the other was maintained at ambient temperature. After 2 days, crystals that were deposited in the cooler arm were filtered, washed with acetone and ether, and dried in air; yield: 66%. Analysis: found: C: 21.00, H: 1.20, N: 6.72%. Calculated for $C_7H_4N_2O_3PbS$: C: 20.82, H: 0.99, N, 6.94%.

2.4. *Synthesis of [Pb(PNO)(N$_3$)]$_n$ (2)*

PNO (0.104 g, 0.75 mmol) was placed in one of the arms of a branched tube [11] whereas lead(II) acetate (0.284 g, 0.75 mmol) and sodium azide (0.049 g, 0.75 mmol) were placed in the other arm. Methanol and water in a ratio of 1 : 2 were carefully added to fill both arms. The tube was then sealed and the ligand-containing arm was immersed in a bath at 60 °C whereas the other was maintained at ambient temperature. After three days, crystals that were deposited in the cooler arm were filtered, washed with mother liquor and dried in air; yield: 67%. Analysis: found: C: 19.20, H: 1.09, N: 14.35%. Calculated for $C_6H_4N_4O_3Pb$: C: 18.59, H: 1.03, N, 14.46%.

3. Results and discussion

3.1. *Spectroscopic studies*

Two coordination polymers are synthesized using HPNO and lead acetate with different pseudohalides (thiocyanate and azide) and are formulated as $[Pb(PNO)(NCS)]_n$ (**1**) and $[Pb(PNO)(N_3)]_n$ (**2**). In numerous instances, a change in stoichiometry from PbX_2L to PbX_2L_2, where X is an anion and L is a bidentate ligand such as 2,2′-bipyridine or 1,10-phenanthroline, is associated with a change from a lattice composed of oligomeric or polymeric entities to a lattice composed of molecular species [12]. Yet, all attempts to synthesize new polymers by changing stoichiometry of reactants were ineffective. IR spectra displayed characteristic absorption bands for picolinate *N*-oxide, thiocyanate, and azide. The relatively weaker absorption bands around 3025–3030 cm^{-1} are due to the C–H modes involving the aromatic ring hydrogens of **1** and **2**, respectively. Absorptions with variable intensity at 1400–1620 cm^{-1} correspond to aromatic ring vibrations of PNO anion [13]. For **1** and **2**, the two strong absorptions at ca. 1590, 1590 and 1385, 1400 cm^{-1} are assignable to $\nu_{as}(COO)$ and $\nu_s(COO)$ of PNO anions, respectively [14]. The IR spectra display very strong absorption at 2050 cm^{-1} due to $\nu(C{\equiv}N)$ of the coordinated thiocyanato groups. The observed $\nu(C{\equiv}N)$ frequencies for the complexes are most consistent with N-bonded thiocyanate (for S-bonded thiocyanate, the $\nu(C{\equiv}N)$ frequencies ranging from 2110 to 2140 cm^{-1}, whereas in *N*-bonded thiocyanate, the $\nu(C{\equiv}N)$ is less than 2110 cm^{-1} [15, 16]), which is also confirmed by X-ray studies (Section 2.3). The peaks at 2100 (vs) and 1292 (m) cm^{-1} are assigned as (ν_{as}-N_3) and (ν_s-N_3), respectively, consistent with asymmetric bridging (μ-N_3) [17]. The ^1H NMR spectrum of DMSO solution of **1** and **2** at 7.40–8.25 ppm display four different signals of protons of picolinate *N*-oxide anion.

3.2. *Thermal studies*

TGA were performed on polycrystalline samples under nitrogen. Compounds **1** (see for example in figure 1S) and **2** are thermally stable to 180 °C. Thermal decompositions follow three steps from 180 to 600 °C from decomposition of PNO^-, thiocyanate, and azide. Mass loss calculations and microanalyses of the solid residues suggest a final decomposition product of the complexes at 600 °C is PbO with total mass loss of 48.10% for **1** (Calcd 50.33%) and 54.16% for **2** (Calcd 57.57%), respectively, agreeing with the proposed structures. It is possible that these compounds are source precursors for lead oxide materials.

3.3. *Descriptions of crystal structures of $[Pb(PNO)(NCS)]_n$ (1) and $Pb(PNO)(N_3)]_n$ (2)*

The single-crystal X-ray diffraction analysis reveals that **1** crystallized in the orthorhombic chiral space group $P2_12_12_1$. The asymmetric unit of **1** consists of one Pb^{II}, one PNO, and one thiocyanate. Each Pb^{II} is six-coordinate with two μ_2-O atoms from *N*-oxide, three carboxylate oxygens (O_{COO^-}) from two PNO, and one nitrogen of thiocyanate (see figure 1). Five oxygens and one nitrogen are located on one side of Pb^{II}, which adopts a hemidirected structure [11], suggesting the presence of a stereochemically active lone electron pair around Pb^{II}. Each Pb in this structure with six normal bonds form another two "weak" Pb···S interactions {$Pb1\cdots S1^{iii}$ (iii: $-0.5+x$, $0.5-y$, $-z$) = 3.042(4) Å and $Pb1\cdots S1^{iv}$ (iv: $-0.5+x$, $-0.5-y$, $-z$) = 3.678(8) Å (these distances have been considered as bonds [15])}. In **1**, PNO^{-} is a triconnector linking three Pb^{II} centers; $O_{N\text{–}O}$ and O_{COO^-} [18] act as a diconnector to link two Pb^{II} centers. Lead(II) centers are bridged by two thiocyanates as μ-1,3,3 (μ-N,S,S) bridges (if, distances of Pb···S are considered as a bond) (figure 2). $O_{N\text{–}O}$ and O_{COO^-} of PNO bridging two leads as zig-zag Pb_2O_2 units (Pb···Pb with distances of 4.271 Å) link to form a one-dimensional (1-D) coordination polymer, which is then further extended into a 2-D layer by bridging thiocyanates (Pb···Pb with distances of 6.820 Å) (figure 3) [19]. The overall network topology can be described as a four-connected network. The Schlafli symbol for the net is ($4^2.6^2$).

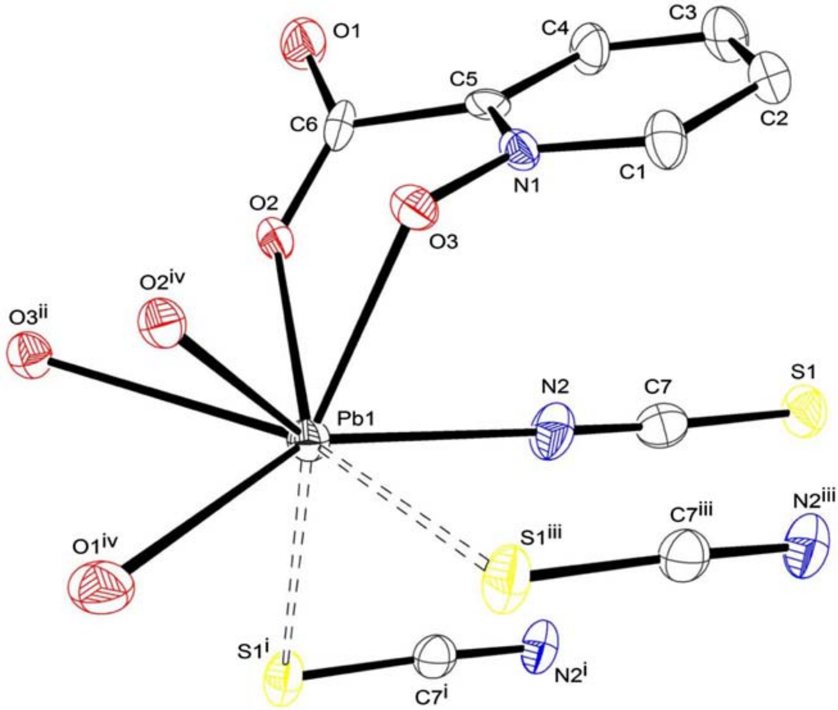

Figure 1. ORTEP diagram of **1** with thermal ellipsoids at 40% probability and atom numbering scheme indicating coordination sphere of lead(II). Symmetry codes: i: $0.5+x$, $-0.5-y$, $-z$; ii: $0.5+x$, $0.5-y$, $-z$; iii: $-0.5+x$, $0.5-y$, $-z$; iv: $-0.5+x$, $-0.5-y$, $-z$.

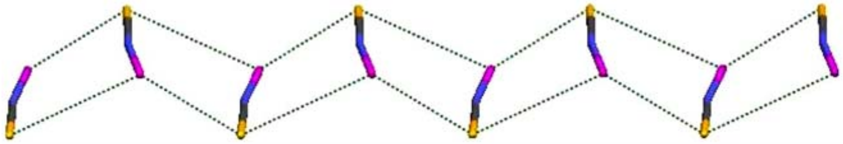

Figure 2. View of the thiocyanate coordination mode in **1** (Pb: gray, N: blue, S: yellow). (see http://dx.doi.org/10.1080/00206814.2013.772145 for color version.)

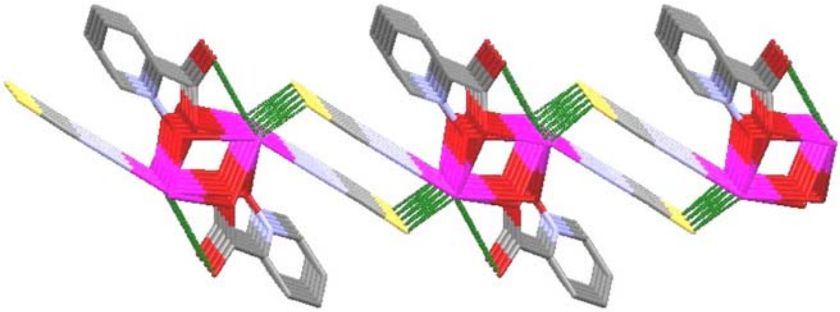

Figure 3. Perspective view of the 2-D coordination polymer networks in **1**, along the *a*-axis.

Single-crystal X-ray structural analysis shows that **2** is a 2-D open framework in which the asymmetric unit contains one Pb^{II}, one PNO, and one azide. Each Pb^{II} is eight-coordinate with two μ-O from two *N*-oxides, three carboxylate oxygens (O_{COO^-}) [18] from two PNO, and three nitrogens of three azides (see figure 4). The arrangement of PNO and azide suggests a gap in the coordination around the metal, possibly occupied by a stereo-active lone pair of electrons on lead(II) [20]. The observed shortening of the Pb–O bond opposite to

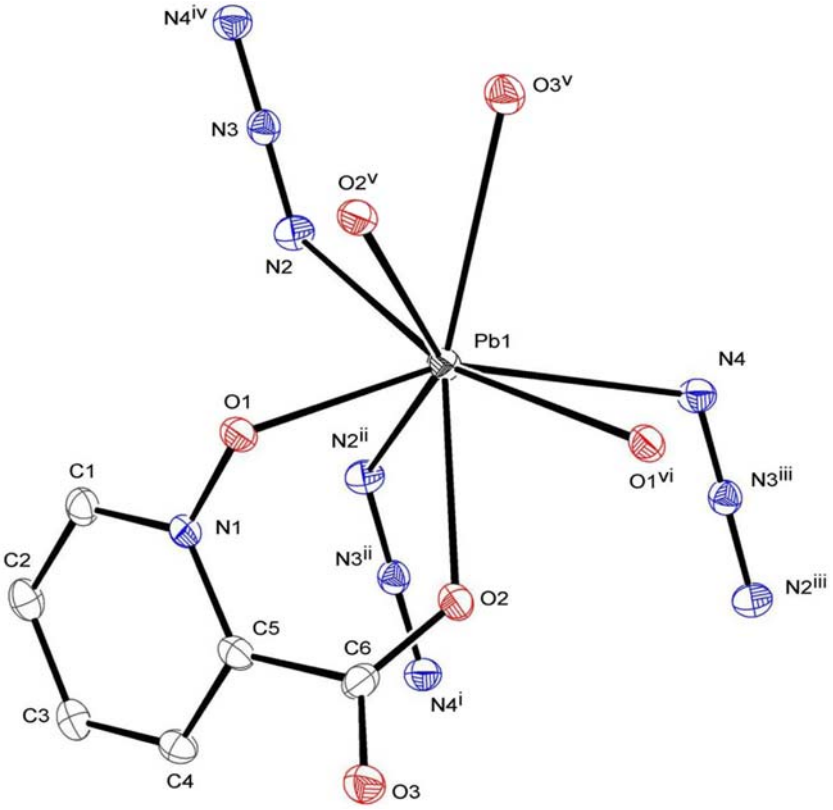

Figure 4. ORTEP diagram of **2** with thermal ellipsoids at 40% probability and atom numbering scheme indicating coordination sphere of lead(II). Symmetry codes: i: $-1-x$, $-1-y$, $-1-z$; ii: x, $1+y$,$+z$; iii: $-1-x$, $0.5+y$, $-1.5-z$.

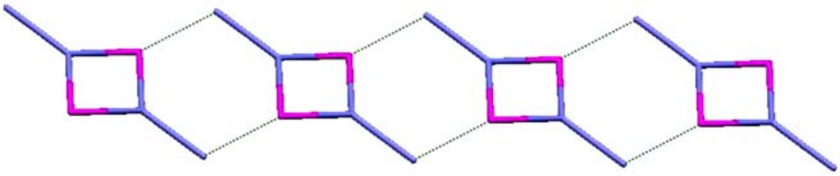

Figure 5. View of the azide coordination mode in **2** (Pb: gray, N: blue). (see http://dx.doi.org/10.1080/00206814.2013.772145 for color version.)

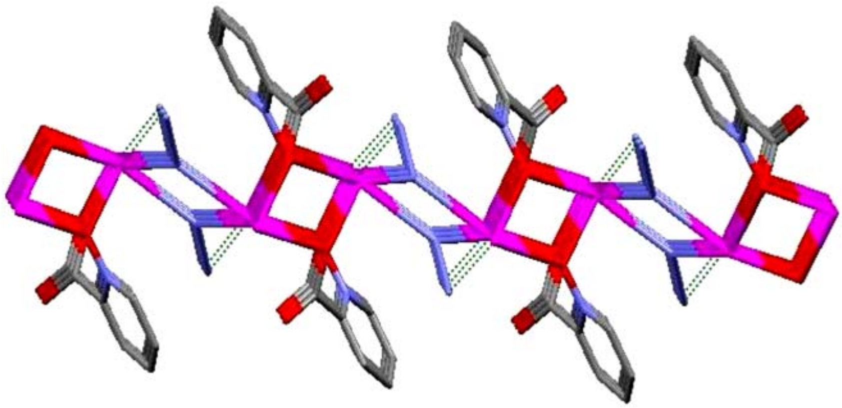

Figure 6. Perspective view of the 2-D coordination polymer networks in **2**, along the *b*-axis.

the putative lone pair (Pb1–O1 = 2.387(4) Å compared with Pb1–O3^{v} = 2.937(4) Å adjacent to the lone pair) supports this [21]. The lead(II) centers are bridged by azides as μ-1,1,3 (μ-*N*,*N*,*N*), a common coordination mode of azide [22] and different from a similar compound [2] (figure 5). In fact, Pb^{II} are bridged by two fashions [Pb···Pb with distances of 5.884 Å for μ-1,3 (μ-*N*,*N*) and 4.372 Å for μ-1,1 (μ-*N*,*N*)] of azide. In **2**, PNO is a triconnector to link three Pb^{II} centers: $O_{N–O}$ and O_{COO^-} bridge two leads and chelate, respectively. $O_{N–O}$ of PNO bridges as Pb_2O_2, while $O_{N–O}$ of PNO in a copper(II) compound [2] is monodentate. Topology of 2-D lead(II) coordination polymers without intermolecular interactions can be described as a three-connected network. The Schlafli symbol for the net is (6.3). Bridging PNO not only links leads, but also creates two kinds of 3-D channels with different dimensions (figure 6).

Table 3. Intermolecular interactions for **1** and **2**.

A···H–B	A···H/Å	A···B/Å	A···H–B/°
1			
C1–H1A···N2 (−1 + *x*, *y*, *z*)	2.673	3.587	168.28
C3–H3A···O1 (−*x*, 1/2 + *y*, −1/2 − *z*)	2.613	3.164	118.48
C2–H2A···O1 (1 − *x*, 1/2 + *y*, −1/2 − *z*)	2.704	3.378	130.05
C4–H4A···O1 (−*x*, 1/2 + *y*, −1/2 − *z*)	2.707	3.210	114.78
O1···S1 (*x*, 1 + *y*, *z*)		3.260	
2			
C3–H3A···N4 (1 + *x*, −1/2 − *y*, 1/2 + *z*)	2.463	3.371	159.96
C1–H1A···N4 (−1 − *x*, −*y*, −1 − *z*)	2.478	3.167	129.36
C4–H4A···O3 (−*x*, −2 − *y*, −1 − *z*)	2.448	3.301	149.36
C1–H1A···O2 (*x*, 1 + *y*, *z*)	2.712	3.532	144.92

Inspection of the data of **1**and **2** for weak directional intermolecular interactions by Mercury software [23], which was used for calculating supramolecular interactions, shows C–H···O and C–H···N interactions (table 3) [15]. In crystal packing of **1** and **2**, 3-D supramolecular networks are constructed by C–H···O and C–H···N interactions that are substantially shorter than the van der Waals distances, 2.77 Å for the H···O distance and 2.67 Å for H···N distance [24].

4. Conclusion

We have prepared two coordination polymers that crystallize in the space groups $P2_12_12_1$ and $P2_1/c$, based on PNO, pseudohalides, and lead. Three factors including lone pair activity, weak directional intermolecular interactions, and placement of ligands control the coordination spheres of the Pb(II) complexes. Whether lone-pair activity stretches coordinative bonds to result in ligand interactions or intermolecular interactions which impose a positioning of the donor atoms to form a gap in the coordination sphere remains a question. Due to tridentate bridging PNO and the presence of different pseudohalides (thiocyanate and azide bridges as μ-1,3,3 (μ-N,S,S) and μ-1,1,3 (μ-N,N,N), respectively), **1** and **2** present 2-D nets. Abundant weak interactions such as C–H···O and C–H···N interactions between ligands of 2-D coordination polymers provide additional assembly forces leading to a 3-D supramolecular network for both **1** and **2** [25].

Acknowledgments

Support of this investigation by Payame Noor University and Iran National Science Foundation, INSF, is gratefully acknowledged by F.M. H.K.F. and C.K.Q. would like to thank Universiti Sains Malaysia (USM) for the Research University Grant (No. 1001/PFIZIK/811160). The authors extend their appreciation to The Deanship of Scientific Research at King Saud University for the funding the work through the research group project No. RGP-VPP-207.

References

[1] (a) J.G. Lin, Y. Su, Z.F. Tian, L. Qiu, L.L. Wen, Z.D. Lu, Y.Z. Li, Q.J. Meng. *Cryst. Growth Des.*, **7**, 2526 (2007); (b) S.K. Ghosh, P.K. Bharadwaj. *Inorg. Chem.*, **44**, 3156 (2005); (c) X.W. Wang, Y.R. Dong, Y.Q. Zheng, J.Z. Chen. *Cryst. Growth Des.*, **7**, 613 (2007); (d) Z.G. Li, G.H. Wang, H.Q. Jia, N.H. Hu, J.W. Xu, *Cryst EngCommun.*, **9**, 882 (2007).
[2] Q. Gao, Y.-B. Xie, M. Thorstad, J.-H. Sun, Y. Cui, H.-C. Zhou. *CrystEngCommun.*, **13**, 6787 (2011).
[3] (a) W.P. Wu, Y.-Y. Wang, Y.-P. Wu, J.-Q. Liu, X.-R. Zeng, Q.-Z. Shi, S.-M. Peng. *Cryst. Eng. Commun.*, **9**, 753 (2007); (b) W. Gui. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **63**, m3168 (2007).
[4] S. Lis, Z. Piskula, M. Kubicki. *Mater. Chem. Phys.*, **114**, 134 (2009).
[5] (a) B.-P. Yang, J.-G. Mao, Z.-C. Dong. *Inorg. Chem. Commun.*, **7**, 104 (2004); (b) E. Bermejo, A. Castineiras, R. Dominguez, J. Strahle, C. Maichle-Mossmer. *Polyhedron*, **15**, 1923 (1996).
[6] Z. He, Z.-M. Wang, C.-H. Yan. *CrystEngCommun*, **7**, 143 (2005).
[7] F. Marandi, P. Hassanmohammadi, H.-K. Fun, C.K. Quah. *Z. Anorg. Allg. Chem.*, **638**, 461 (2012).
[8] Bruker. *APEX2 Version 1.27, SAINT Version 7.12a and SADABS Version 2004/1*, Bruker AXS Inc., Madison, Wisconsin, USA (2005).
[9] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).
[10] L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).
[11] F. Marandi, F. Amoopour, I. Pantenburg, G. Meyer. *J. Mol. Struct.*, **973**, 124 (2010).
[12] A.A. Soudi, F. Marandi, A. Morsali, G.P.A. Yap. *J. Coord. Chem.*, **59**, 1139 (2006).

[13] W.-Y. Yin, X.-Y. Tang, J. Yang, Y.-S. Ma, R.-X. Yuan. *J. Coord. Chem.*, **63**, 1157 (2010).

[14] "HKL2000" and "maXus" softwares, University of Glasgow, Glasgow, Scotland, U.K., Nonius BV, Delft, The Netherlands and MacScience Co. Ltd., Yokohama, Japan (2000).

[15] F. Marandi, M. Mottaghi, G. Meyer, I. Pantenburg. *Z. Anorg. Allg. Chem.*, **635**, 165 (2009).

[16] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, Wiley, New York (1986) and Part B 5th Edn. (1997).

[17] M.A.M. Abu-Youssef. *Polyhedron*, **24**, 1829 (2005).

[18] (a) Z. Sun, L.-M. Fan, W. Zhang, D.-C. Li, P.-H. Wei, B. Li, G.-Z. Liu, L.-J. Tian, X.-T. Zhang. *J. Coord. Chem*., **65**, 1847 (2012); (b) Z.-H. Lei, Y.-E. Cha, X. Li, K. Zhao. *J. Coord. Chem*., **65**, 1592 (2012); (c) L.-D. Wang, F. Tao, M.-L. Cheng, Q. Liu, W. Han, Y.-J. Wu, D.-D. Yang, L.-J. Wang. *J. Coord. Chem*., **65**, 923 (2012); (d) Z. Wang, Q. Wei, G. Xie, Q. Yang, S. Chen, S. Gao. *J. Coord. Chem*., **65**, 286 (2012).

[19] F. Marandi, J. Sartaji, G. Bruno, H. Aamiri-Rudbari. *J. Coord. Chem.*, **65**, 1872 (2012).

[20] F. Marandi, Z. Nikpey, J.H. Goh, H.-K. Fun. Z. Naturforsch., **65b**, 128 (2010).

[21] L. Shimoni-Livny, J.P. Glusker, C.W. Brock. *Inorg. Chem.*, **37**, 1853 (1998).

[22] F. Marandi, B. Mirtamizdoust, S. Chantrapromma, H.-K. Fun. *Z. Anorg. Allg. Chem.*, **633**, 1329 (2007).

[23] *MERCURY 1.4.1*, *Copyright Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge, CB2 1EZ, UK (2001–2005).

[24] G. Althoff, J. Ruiz, V. Rodriguez, G. Lopez, J. Perez, C. Janiak. *CrystEng Commun.*, **8**, 662 (2006).

[25] (a) L.-L. Wu, H.-H. Song. *J. Coord. Chem*., **65**, 2135 (2012); (b) J. Hu, S. Li, J. Zhao, S. Chen, H. Hou, H. Zhao. *J. Coord. Chem*., **65**, 1258 (2012).