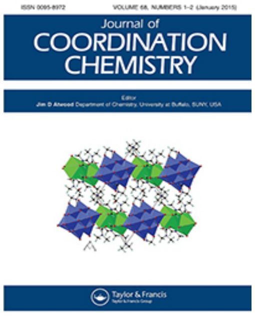

Journal of COORDINATION CHEMISTRY

Taylor & Francis
Taylor & Francis Group

Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

Synthesis, structural characterization, and solution properties of a 1-D Pb(II)-bipyridine coordination polymer

Dhananjay Dey, Hare Ram Yadav, Abhranil De, Sourav Chatterjee, Milan Maji, Angshuman Roy Choudhury, Niranjan Kole & Bhaskar Biswas

To cite this article: Dhananjay Dey, Hare Ram Yadav, Abhranil De, Sourav Chatterjee, Milan Maji, Angshuman Roy Choudhury, Niranjan Kole & Bhaskar Biswas (2015) Synthesis, structural characterization, and solution properties of a 1-D Pb(II)-bipyridine coordination polymer, Journal of Coordination Chemistry, 68:1, 169-180, DOI: 10.1080/00958972.2014.985215

To link to this article: http://dx.doi.org/10.1080/00958972.2014.985215

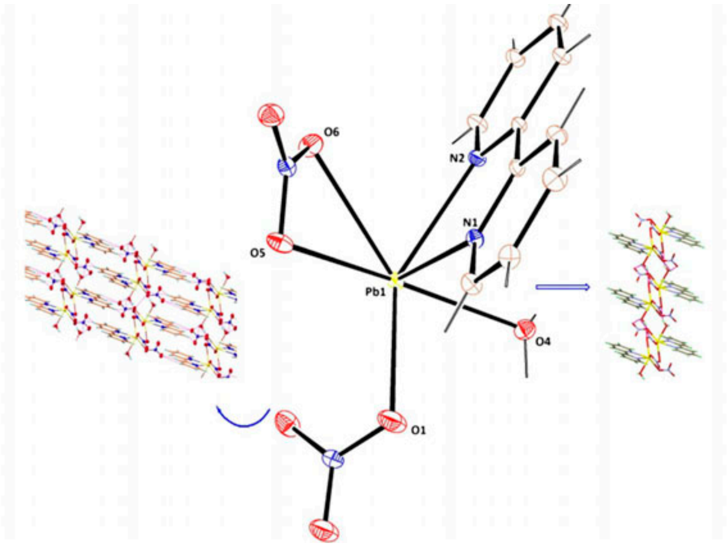
Journal of Coordination Chemistry, 2015
Vol. 68, No. 1, 169–180, http://dx.doi.org/10.1080/00958972.2014.985215

Synthesis, structural characterization, and solution properties of a 1-D Pb(II)-bipyridine coordination polymer

DHANANJAY DEY[†], HARE RAM YADAV[‡], ABHRANIL DE[†],
SOURAV CHATTERJEE[§], MILAN MAJI[¶], ANGSHUMAN ROY CHOUDHURY[‡],
NIRANJAN KOLE[†] and BHASKAR BISWAS[*][†]

[†]Department of Chemistry, Raghunathpur College, Purulia, India
[‡]Department of Chemical Sciences, Indian Institute of Science Education and Research, Mohali, India
[§]Laboratory of Catalysis and Chemical Biology, Department of Chemistry, CSIR-Indian Institute of Chemical Biology, Kolkata, India
[¶]Department of Chemistry, National Institute of Technology, Durgapur, India

(*Received 15 May 2014; accepted 8 October 2014*)



A new one-dimensional (1-D) Pb(II) coordination polymer, [Pb(2,2′-bpy)$(NO_3)_2(H_2O)]_n$ (**1**) (2,2′-bpy = 2,2′-bipyridine), has been synthesized and characterized by different spectroscopic techniques and X-ray single-crystal analysis. From the X-ray crystal structure of **1**, the Pb^{2+} can be best described as a highly distorted pentagonal bipyramid with O4 (water) and O6 (nitrate) at apical positions (∠O4–Pb–O6 of 143.7(1)°). Variability in bond distances reveals that Pb^{2+} is unsymmetrically surrounded by two nitrates, one 2,2′-bpy and one water. Nitrates bridge between monomers. The molecule crystallizes in the monoclinic $P2_1/n$ (14) space group. This is the first example of a 1-D Pb(II) polymer in which nitrates show three different coordination motifs (terminal, chelating, and bridging). Solid state as well as solution phase UV–vis spectral analysis and mass spectrometric

---

[*]Corresponding author. Emails: mr.bbiswas@rediffmail.com, icbbiswas@gmail.com

studies clearly reveal instability with breakdown of Pb(II) polymer in aqueous solution. The arrangement of the 2,2′-bpy, water, and nitrates leaves a coordination gap at the Pb(II) occupied probably by a stereo-active lone pair of electrons.

Keywords: Pb(II); X-ray crystal structure; 1-D polymer; Supramolecular interactions; Spectroscopic investigation

1. Introduction

The tendency of heavier main group elements to adopt an oxidation state below the highest possible oxidation state has been attributed to the effect of the “inert electron-pair” [1]. This property was explained by the relativistic stabilization of the 6s orbital, caused by direct relativistic effect and the presence of the filled 4f subshell. Pb(IV) compounds are strong oxidants in aqueous systems, spontaneously reduced to Pb(II) with the formation of oxygen gas. The broad range of coordination numbers from 2 to 12 exhibited by Pb(II), if counting all nearest neighbors, results in a large variety of configurations of its compounds [2, 3]. In terms of coordination number, the hybrid orbital with a lone electron pair can be considered an additional ligand in the coordination sphere, taking up more space than that of an ordinary ligand [4]. However, according to molecular orbital theory, the classical conception of 6s/6p orbital hybridization on the Pb(II) is regarded as incorrect. This is because the energy levels of these orbitals are too dissimilar, and the different spatial distribution of their corresponding wave functions [5–7]. Instead, the stereochemical activity observed in Pb(II) complexes should be seen as a result of an antibonding lead 6s-ligand np (6s/np) interaction which causes structural distortions to energetically minimize these unfavorable covalent interactions [5–7].

Two general structural types of Pb(II) complexes are identified, *hemidirected,* and *holodirected*, as proposed by Shimoni-Livny *et al.* [8]. In the former, the electron distribution around the metal ion is unevenly distributed, caused by antibonding metal–ligand interactions creating a gap in the coordination sphere, while in the latter, the electron distribution as well as the coordination sphere is symmetric. Jin *et al.* and Morsali *et al.* reported different 1-D–3-D Pb(II) coordination polymers containing N-donor auxiliary ligands with different topological views [9].

The increasing use of Pb(II) in industry, such as in paints and batteries [10], pollutes the environment and has damaging effects on human health. Therefore, investigation of the coordination chemistry of Pb and its complexes attracts interest from inorganic and coordination chemists for the development of practical ligands as extractants, lead-poisoning treatment agents, and sensors [11]. To introduce N-donor organic ligands and counter anions is an important strategy for constructing coordination polymers which are guided by precise topological control through manipulation of weak intermolecular interactions and leading to different dimensions of the frameworks [12]. Hence, we synthesized a 1-D Pb(II) coordination polymer (**1**) containing bipyridine, nitrate ion, and water as co-ligands. The physicochemical properties of **1** have been investigated through different spectroscopic techniques. To the best of our knowledge, this is the first example of mixed-ligand 1-D Pb(II) polymer in which nitrate shows three different coordination motifs (terminal, chelating, and bridging).

2. Experimental

2.1. *Preparation of the complex*

2.1.1. Chemicals, solvents, and starting materials. High purity 2,2′-bipyridine (Lancaster, UK), ammonium ceric nitrate (Aldrich, UK), and lead nitrate (E. Merck, India) were purchased and used without purification. All the other reagents and solvents are of analytical grade (A.R. grade), purchased from commercial sources and used as received.

2.1.2. General procedure for the synthesis of Pb(II) polymer (1). A 60–40 v/v AcOH–H_2O solution (10 cm^3) of 2,2′-bipyridine (0.156 g, 1 mM) was added dropwise to a solution of $Pb(NO_3)_2$ (0.331 g, 1 mM) in the same solvent (10 cm^3) and mixed slowly on a magnetic stirrer with slow stirring for 30 min. The whole solution remains colorless while stirring was continued for another 10 min. The clear solution was filtered, and the supernatant liquid was kept in air for slow evaporation. After few days, fine microcrystalline compound that separated out was washed with hexane and dried in vacuo over silica gel indicator. Yield: 0.258 g (77.9% based on metal salt) Anal. Calcd for $C_{10}H_{10}N_4O_7Pb$ (**1**): C, 23.76; H, 1.99; N, 11.09. Found: C, 23.81; H, 1.92; N, 11.10. IR (KBr pellet, cm^{-1}): 3414, 1602, 1583 ($\nu_{C=N}$), 1384 (ν_{NO3}), 852; UV–vis (λ_{max}, nm): 238, 255–274.

2.2. *Physical measurements*

Infrared spectrum (KBr) was recorded with a FTIR-8400S SHIMADZU spectrophotometer from 400 to 3600 cm^{-1}. ^1H NMR spectrum in DMSO-d_6 was obtained on a Bruker Avance 300 MHz spectrometer at 25 °C and was recorded at 299.948 MHz. Chemical shifts are reported with reference to $SiMe_4$. Ground-state absorption measurements were made with a Jasco model V-530 UV–vis spectrophotometer. Solid state UV–vis analysis was recorded on an Agilent Cary 5000 UV1204M050 Spectrometer. Thermal analysis was carried out on a PerkinElmer Diamond TG/DTA system to 900 °C in a static nitrogen atmosphere with a heating rate of 10 °C/min. Elemental analyses were performed on a PerkinElmer 2400 CHN microanalyzer. Electrospray ionization (ESI) mass spectrum was recorded on a Q-TOF Micro^{TM} Mass Spectrometer.

2.3. *X-ray diffraction study*

Single-crystal X-ray diffraction data were collected using a Rigaku XtaLABmini (Fixed 2Theta and Distance) diffractometer equipped with a Mercury375R (2 × 2 bin mode) CCD detector. The data were collected with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71075$ Å) at 293 K using ω scans. The data were reduced using Crystal Clear suite (Reference *CrystalClear 2.0*; Rigaku Corporation: Tokyo, Japan), and the space group determination was done using Olex2. The structure was resolved by direct methods and refined by full-matrix least-squares procedures using the SHELXL-97 software package using the OLEX2 suite [13, 14].

2.4. *Thermogravimetric analysis of 1*

The thermal behavior of the lead polymer (**1**) was followed up to 700 °C in a static nitrogen atmosphere with a heating rate of 10 °C per minute.

3. Results and discussion

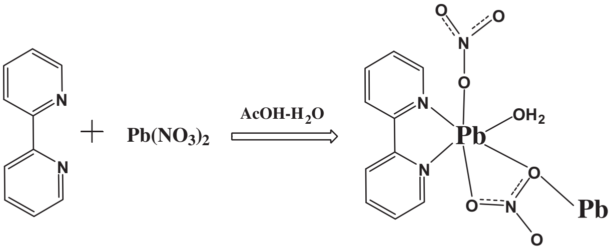
3.1. *Syntheses and formulation*

The polymeric 1-D Pb(II) complex was prepared by mixing Pb(II) nitrate and 2,2′-bipyridine in acetic acid–water. The coordination geometry of **1** was determined by single-crystal X-ray diffraction along with different spectroscopic and analytical techniques. Colorless crystals suitable for X-ray data collection were obtained by slow evaporation of resultant reaction mixture. The formulation was confirmed by elemental analysis, IR, UV–vis, ^{1}H NMR, mass spectral analysis, and X-ray structural analysis of the Pb(II) polymer. The schematic presentation of synthesis is given in scheme 1.

The NMR spectrum of Pb(II) polymer is recorded to characterize **1** in DMSO-d_6 solution using tetramethylsilane as an internal standard. The heterocyclic bipyridine-H appeared from ~8.4 to 6.6 ppm (figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.985215). The characteristic signals at 8.4 ppm indicate the closest proton to imine of the bipyridine, and all aromatic-CH proton signals are in the range of 7.3–6.6 ppm.

3.2. *Description of crystal structure and supramolecular interactions*

The X-ray structural determination of **1** reveals a 1-D polymeric neutral Pb(II) complex with the space group $P2_1/n$. An ORTEP view of the asymmetric unit of the lead complex is shown in figure 1 and μ_2-nitrato-Pb(II) polymer with an atom-labeling scheme is shown in figure 2. A summary of the crystallographic data and structure refinement parameters for **1** is given in table 1, and the bond angle and distance data are given in table 2. The crystal structure of **1** consists of nitrate-O bridged monomeric units of $[Pb(2,2'\text{-bpy})(NO_3)_2(H_2O)]_n$. Each lead is chelated by two nitrogens of the bpy ligand with Pb–N distances of 2.504(4) and 2.546(4) Å. The nitrates also formed a chelate with Pb through Pb–O bond (Pb–O distances are 2.658(5), 2.797(4), and 2.934(4) Å). One nitrate also forms a bridge between two metal centers, by mono-coordinated oxygen of nitrate with Pb and also by mono-coordinated oxygen of water (table 2). The coordination number of Pb(II) in this polymer is



Scheme 1. Preparative procedure of Pb(II) polymer (**1**).

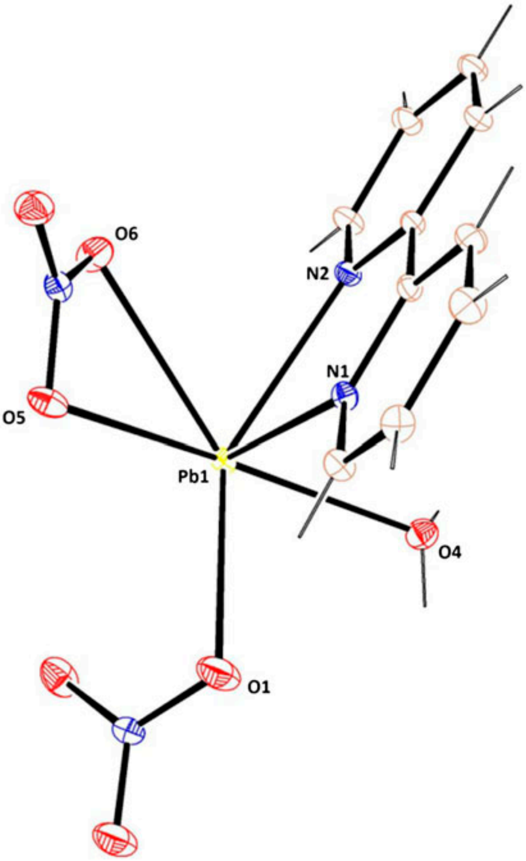


Figure 1. ORTEP diagram of asymmetric unit in $[Pb(2,2'\text{-bpy})(NO_3)_2(H_2O)]_n$ (**1**) (30% ellipsoid probability) with atom-numbering scheme.

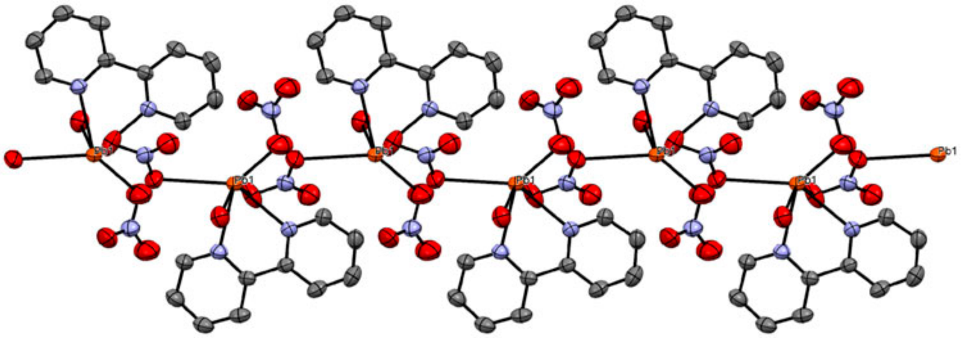


Figure 2. Formation of 1-D polymer $[Pb(2,2'\text{-bpy})(NO_3)_2(H_2O)]_n$ (**1**) along the crystallographic *b* axis. Hydrogens are removed for clarity.

Table 1 Crystallographic data of [Pb(2,2′-bpy)$(NO_3)_2(H_2O)]_n$ (**1**).

Parameters	**1**
CCDC number	1001948
Empirical formula	$C_{10}H_{10}N_4O_7Pb$
Formula weight	505.42
Temperature (K)	293
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	7.2586(7)
b (Å)	9.9067(9)
c (Å)	19.3404(17)
Volume (Å^3)	1390.1(2)
Z	4
Z'	1
ρ (g cm^{-3})	2.415
μ (mm^{-1})	12.180
F(0 0 0)	944
Index ranges	−9,9; −12,12; −25,25
θ ranges (°)	3.0–27.5
Total reflections	13,877
Unique reflections	3178
R_1 [$I > 2\sigma(I)$]	0.0289, 0.0734
R_{int}	0.0435
wR_2 (all data)	0.0734
GooF	1.062
Largest peak and hole (e Å^{-3})	−1.80, 1.60

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

Bond distances			
Pb1–O1	2.659(6)	Pb1–O4	2.475(4)
Pb1–O2	3.029(4)	Pb1–O5	2.934(4)
Pb1–O6	2.797(4)	Pb1–O5*	2.859(4)
Pb1–N1	2.504(4)	Pb1–O7*	3.018(5)
Pb1–N2	2.545(4)		
Bond angles			
O1–Pb1–O2	43.36(16)	O2–Pb1–O4	106.74(14)
O1–Pb1–O4	80.89(15)	O2–Pb1–O5	75.53(13)
O1–Pb1–O5	78.18(14)	O2–Pb–O6	108.89(13)
O1–Pb1–O6	122.10(14)	O2–Pb1–N1	119.05(13)
O1–Pb1–N1	80.72(15)	O2–Pb1–N2	175.34(13)
O1–Pb1–N2	141.29(15)	O2–Pb1–O5*	97.35(12)
O1–Pb1–O5*	130.32(14)	O2–Pb1–O7*	64.88(12)
O1–Pb1–O7*	87.99(14)	O4–Pb1–O5	145.29(12)
O5*–Pb1–O6	95.54(12)	O4–Pb1–O6	143.72(12)
O6–Pb1–O7*	130.58(12)	O4–Pb1–N1	79.42(13)
N1–Pb1–N2	65.10(13)	O4–Pb1–N2	75.67(12)
O5*–Pb1–N1	143.34(12)	O4–Pb1–O5*	86.43(13)
O7*–Pb1–N1	150.57(13)	O4–Pb1–O7*	71.97(12)
O5*–Pb1–N2	78.71(12)	O5–Pb1–O6	43.98(11)
O7*–Pb1–N2	112.76(12)	O5–Pb1–N1	70.13(12)
O5*–Pb1–O7*	42.60(12)	O5–Pb1–N2	104.86(12)
O5–Pb1–O7*	133.96(11)	O5–Pb1–O5*	128.11(12)
O6–Pb1–N1	77.65(13)	O6–Pb1–N2	69.29(11)

*Indicates usual crystallographic significance, i.e. opposite atom symmetry (when symmetric atoms are found in opposite direction centered at metal ion generally * is used).

seven. The interaction of the Pb(II) ions with oxygen of a nitrate of adjacent molecules produces polymeric units in the solid state in a rarely observed 1-D chain and a complex containing three different ligands in the coordination sphere. The distances between the two adjacent Pb centers in the polymeric units are 5.519 Å. The arrangement of the bpy, water, and nitrates suggests a gap or hole in the coordination geometry around the metal ion [∠–O(1)–Pb–O(5) = 130.32°] (occupied probably by a stereo-active lone pair of electrons on Pb(II) (figure 3). The observed shortening of the Pb–N bonds opposite to the presumed lone pair (2.504(4) Å) compared with 2.545(4) Å for the adjacent bond supports the presence of this feature [15] (scheme 2).

Inorganic anions play important roles in inorganic chemistry, atmospheric chemistry, geochemistry, and biochemistry [16]. Chemical, bio-chemical, and natural processes involving inorganic anions in water attract synthetic chemists since the reactivity of the inorganic anions is strongly affected by hydration. Nitrates NO_3^- are common inorganic anions and engaged in many natural processes in water. This Pb(II) polymer is the unique example which consists of two nitrates with three different coordination motifs (terminal, chelating, and bridging) (scheme 3).

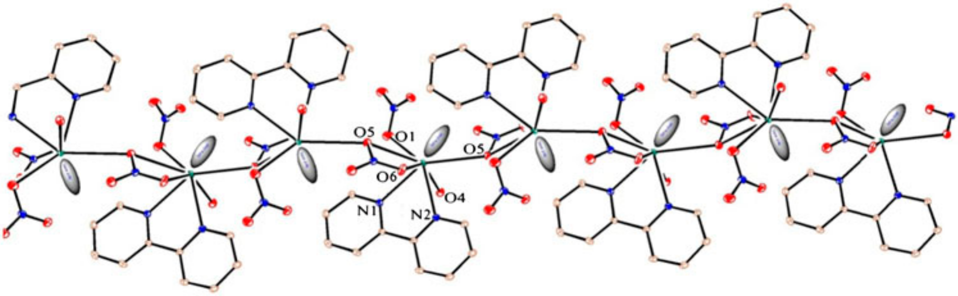
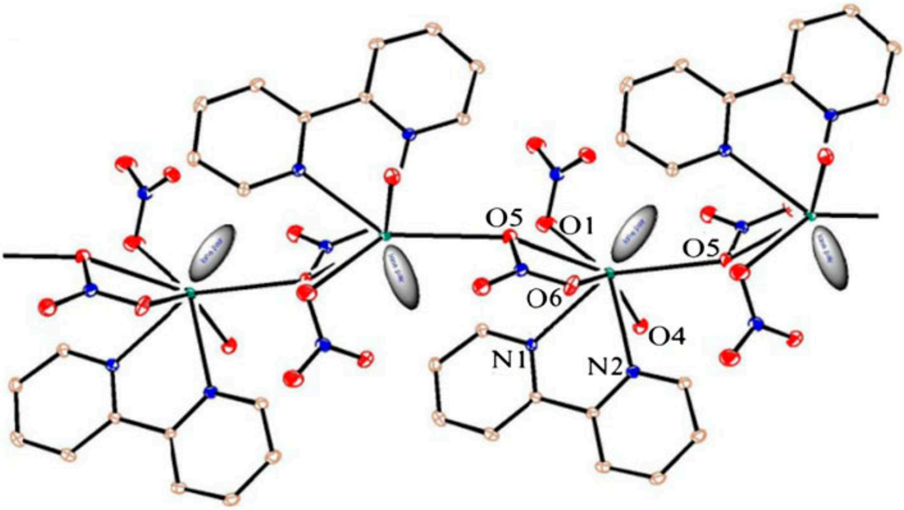
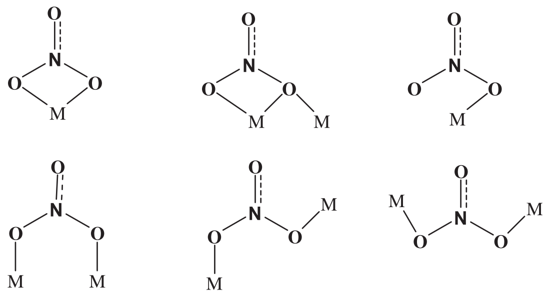


Figure 3. Visualization of nitrate (O1, O3)-bridged 1-D polymer $[Pb(2,2'\text{-bpy})(NO_3)_2(H_2O)]_n$ (**1**) reflecting stereochemically active lone pair on Pb(II) ion and its hemidirected nature.



Scheme 2. Hemidirected nature of **1**.



Scheme 3. Possible coordination motifs of nitrate.

In the polymeric [Pb(2,2′-bpy)$(NO_3)_2(H_2O)]_n$ complex, there are two nitrates with one nitrate making a highly strained four-member chelate ring (∠O5–Pb1–O6 = 43.9°) to Pb(II) ions through O–O coordination and another one makes terminal linkage. Only O5 of the chelating nitrate bridges metal centers to form the polymer and the other nitrate is asymmetrically monodentate toward lead. The three N–O bond lengths and also three bond angles ∠O–N–O of nitrate in [Pb(2,2′-bpy)$(NO_3)_2(H_2O)]_n$ are different, [N(3)–O(5) = 1.254(5), N(3)–O(6) = 1.259(5), N(4)–O(1) = 1.246(6) Å, ∠O(5)–N(3)–O(6) = 117.7(5)°, ∠O(5)–N(3)–O(7) = 120.4(4)°, and ∠O(1)–N(4)–O(2) = 118.8(5)°]. The nitrates are highly distorted

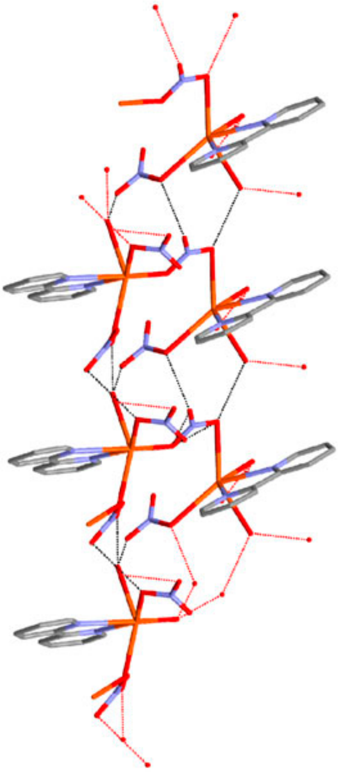


Figure 4. 1-D H-bonded offset structure of **1** along the *b* axis (black dots indicate H-bond interactions; hydrogens are removed for clarity).

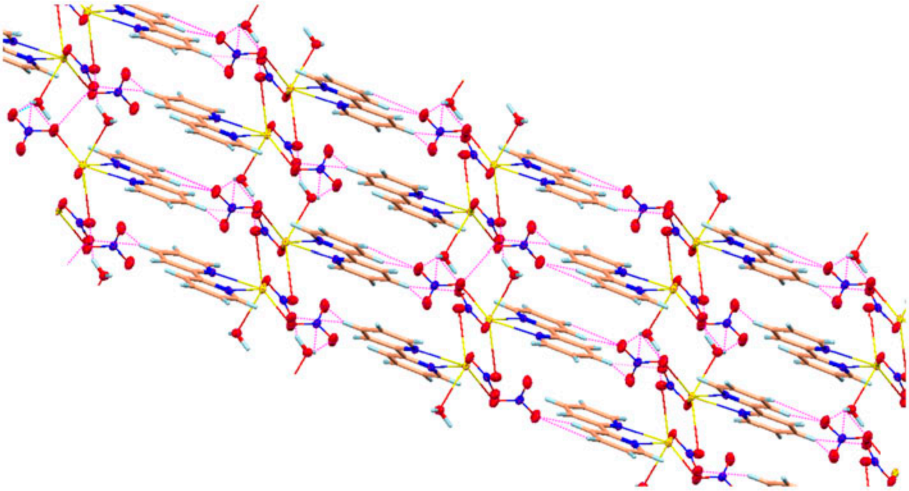


Figure 5. 2-D H-bonded network of the molecules of **1** in the crystal as viewed along the crystallographic *b* axis through C–H···O and O–H···O interactions (pink dotted interaction) (see http://dx.doi.org/10.1080/00958972.2014.985215 for color version).

Table 3. Geometrical parameters of C–H···O and O–H···O hydrogen bonds (Å, °) involved in the supramolecular construction in **1**. D = donor, A = acceptor (Å, °).

D–H···A (Å)	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠D–H···A	Symmetry
C(1)–H(1)...O1	0.93	2.45	3.169	134	x, y, z
C(8)–H(8)...O7	0.93	2.49	3.358	155	$-x+1, -y+1, -z$
C(10)–H(10)...O5	0.93	2.40	3.172	141	$3/2-x, -1/2+y, 1/2-z$
O(4)–H(4A)...O3	0.90	2.40	2.908	162	$5/2-x, -1/2+y, 1/2-z$
O(4)–H(4B)...O6	0.90	2.01	2.783	144	$x+1, +y, +z$

by bridging. For the structure described here, the coordination around lead is hemidirected with a significant gap *trans* to the chelating 2,2′-bipyridine (figure 3) [17].

Close inspection of the crystal structure of Pb(II) polymer reveals that intermolecular hydrogen bonding interactions are responsible for the packing of the complex; π–π stacking interactions are not observed in **1**. Intermolecular hydrogen bonding interactions, O–H···O and C–H···O, are operative in the range from 2.49 to 2.01 Å, indicative of strong to very strong hydrogen bonds. The packing of the molecules of **1** in the solid state exhibits self-assembled structure topologies through different hydrogen bonding modes. The 1-D chain grows along the *b* axis involving O–H···O hydrogen bonds [O(4)–H(4A)···O3, 2.40 Å; O(4)–H(4B)···O3, 2.01 Å; figure 4]. This 1-D chain extends along the *b* axis when C–H···O hydrogen bonds are considered and therefore creates a 2-D network [(C(1)–H(1)···O1, 2.45 Å; C(8)–H(8)···O7, 2.49 Å; C(10)–H(10)···O5, 2.40 Å; figure 5]. All the hydrogen bonding interactions present in **1** are given in table 3.

3.3. *Solution properties of the Pb(II) polymer*

The structural integrity in solution state for polymeric Pb(II) complex has been determined by comparison between solid and solution state UV–vis spectroscopy, ESI, and FAB mass spectral analysis. The Pb(II) polymer is soluble in common solvents like methanol, dichloromethane, acetonitrile, and water.

The Pb(II) polymer shows interesting properties in solid state and solution phase. The UV–vis spectrum for **1** in aqueous medium at room temperature shows a series of high intensity transitions at 200–300 nm and a very broad low energy transition between 450 and 550 nm (figure 6), assigned to the inter-ligand charge transfer transitions among the nitrate and 2,2′-bpy ligands in water [18]. To compare the structural integrity in solid state and solution state, we also recorded an absorbance in solid state. The solid state UV–vis spectrum of **1** showed transitions from 270 to 340 nm and did not produce a band in the visible region (400–800 nm) (figure 7). Dissimilarity in the UV–vis absorbance spectra in aqueous and solid phases reflects that the Pb(II) polymer behaves differently. In aqueous medium, water molecules probably make substantial hydration at the coordination site of Pb(II).

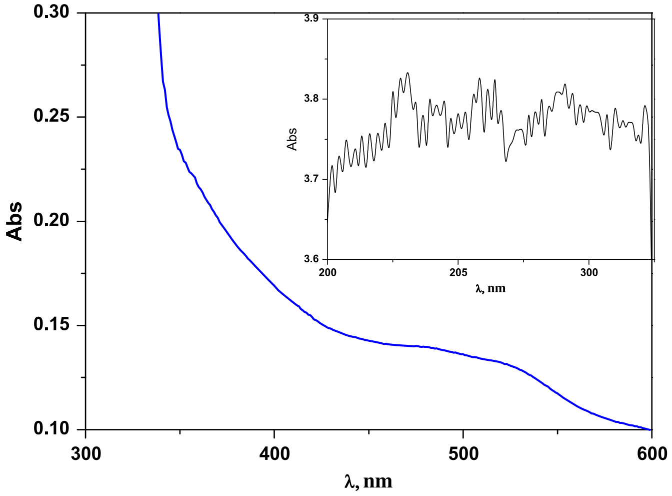


Figure 6. Absorbance spectrum of **1** recorded in aqueous medium (inset: a series of transitions in the region 200–350 nm).

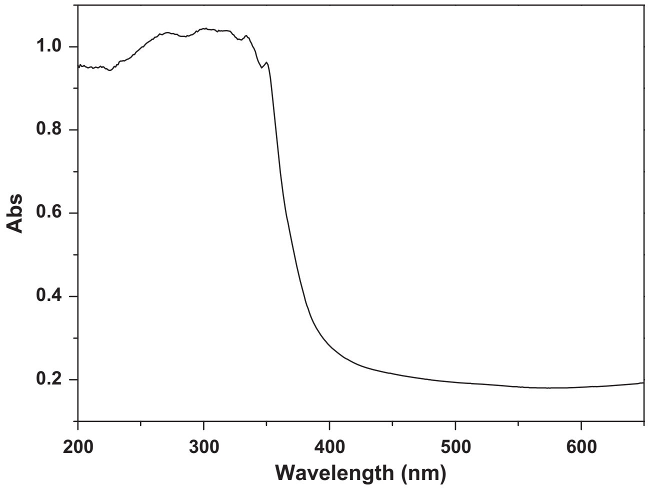


Figure 7. Solid state absorbance spectrum of **1**.

The ESI-MS and FAB mass spectral studies of **1** further consolidate the solution instability. $[Pb(2,2'\text{-bpy})(NO_3)_2(H_2O)]_n$ (**1**) with formula weight 505.42 melts at 117 °C. ESI mass spectral analysis of **1** in aqueous solution exhibits base peak at *m/z* 157.11 for [2,2′-bpy + H^+] (figure S2) whereas FAB mass spectral analysis at 200 °C in solid state produce similar base peak at *m/z* 156 for [2,2′-bpy] (figure S3) but none of the spectra produce molecular ion peak around *m/z* 505.42 in aqueous medium or solid state. The mass spectral analysis reflects that the 1-D Pb(II) coordination polymer immediately break down in aqueous medium or in melted solid state. It is likely the chain structure of the polymer has been broken in aqueous solution.

3.4. *Thermogravimetric analysis*

The thermal behavior of the Pb(II) polymer (**1**) was followed up to 900 °C in a static nitrogen atmosphere with a heating rate of 10 °C per minute. Thermal analysis of the polymer shows that it decomposes in three steps. In the first step, release of coordinated water at 73–91 °C occurs with a mass loss of 4.7% (Calcd 3.56%) (figure S4). In the second step, the mass corresponding to terminal coordinated nitrate and bridging nitrate [expt. mass loss 25.3% (Calcd 24.5%)] are lost from 91 to 296 °C. In the next step, bipy of polymer is lost. The experimental mass losses are in good agreement with theoretical mass loss in all steps.

4. Conclusion

Herein, we report the synthesis, spectroscopic characterization, and single-crystal isolation of a 1-D Pb(II) coordination polymer, $[Pb(2,2'\text{-bpy})(NO_3)_2(H_2O)]_n$ (**1**). From UV–vis and mass spectral analysis in both solid and solution, the coordination polymer is unstable in solution at room temperature and the chain structure breaks down in aqueous medium. This is the first example of a 1-D Pb(II) polymer in which nitrate shows three different coordination motifs (terminal, chelating, and bridging). The synthesis of **1** enriches the structural varieties of lead complexes and opens possibilities for synthesizing hemidirected lead polymers using different bidentate organic polypyridyl ligands and Pb(II) salts.

Supplementary material

Crystallographic data are available free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) upon request, quoting deposition number CCDC 1001948 for the Pb(II) polymer (**1**).

Acknowledgements

The single-crystal X-ray facility of Department of Chemical Sciences, IISER Mohali is acknowledged for the data collection. Author HRY thankfully acknowledges CSIR, New Delhi, India for the award of Research Fellowship.

Funding

The work is supported financially by the Department of Science and Technology (DST), New Delhi, India under FAST TRACK SCHEME for YOUNG SCIENTIST (NO. SB /FT/CS-088/2013 dtd. 21/05/2014).

References

[1] N.V. Sidgwick, H.M. Powell. *Proc. R. Soc.*, **176**, 153 (1940).
[2] F.H. Allen. *Acta Crystallogr., Sect. B*, **58**, 380 (2002); Cambridge Structural Database (CSD).
[3] *Inorganic Crystal Structure Database*, 1.4.6 (release: 2010-2); FIZ/NIST, Gaithersburg, MD (2010).
[4] R.J. Gillespie, R.S.Q. Nyholm. *Rev. London*, **11**, 339 (1957); R.J. Gillespie, I. Hargittai. *The VSEPR Model of Molecular Geometry*, Allyn and Bacon, Boston, MA (1991).
[5] A.-V. Mudring, In *Inorganic Chemistry in Focus*, 3rd Edn, G. Meyer, D. Naumann, L. Wesemann (Eds), p. 30, Wiley-VCH Verlag, Weinheim (2006).
[6] (a) A.-V. Mudring, F. Rieger. *Inorg. Chem.*, **44**, 6240 (2005); (b) A. Walsh, G.W. Watson. *J. Solid State Chem.*, **178**, 1422 (2005).
[7] A.-V. Mudring. *Eur. J. Inorg. Chem.*, **6**, 882 (2007).
[8] L. Shimoni-Livny, J.P. Glusker, C.W. Bock. *Inorg. Chem.*, **37**, 1853 (1998).
[9] (a) Y.-X. Ren, X.-J. Zheng, L.-P. Jin. *CrystEngComm*, **13**, 5915 (2011); (b) J. Abedini, A. Morsali, R. Kempe, I. Hertl. *J. Coord. Chem.*, **58**, 1719 (2005); (c) A. Morsali, M. Payeghader, S.S. Monfareda, M. Moradi. *J. Coord. Chem.*, **56**, 1719 (2003).
[10] J.S. Casas, J. Sordo (Eds.). *Lead: Chemistry, Analytical Aspects, Environmental Impact and Health Effects*, Elsevier, Amsterdam (2006).
[11] (a) R.C. Gracia, W.R. Snodgrass. *Am. J. Health-Syst. Pharm.*, **64**, 45 (2007); (b) G. Saxena, S.J.S. Flora. *J. Biochem. Mol. Toxicol.*, **18**, 221 (2004); (c) E.S. Claudio, H.A. Godwin, J.S. Magyar. *Prog. Inorg. Chem.*, **51**, 1 (2003).
[12] (a) H. Seko, K. Tsuge, A. Igashira-Kamiyama, T. Kawamoto, T. Konno. *Chem. Commun.*, **46**, 1962 (2010); (b) M.H. Mir, J.J. Vittal. *Angew. Chem., Int. Ed.*, **46**, 5925 (2007); (c) C.N.R. Rao, S. Natarajan, R. Vaidhyanathan. *Angew. Chem., Int. Ed.*, **43**, 1466 (2004); (d) K. Müller-Dethlefs, P. Hobza. *Chem. Rev.*, **100**, 143 (2000); (e) B. Biswas, A. Pal, P. Mitra, F. Tuna, M. Mukherjee, R. Ghosh. *J. Coord. Chem.*, **65**, 4067 (2012); (f) J.M. Lehn. *Science*, **260**, 1762 (1993); (g) B. Biswas, S.-P. Hung, H.-L. Tsai, R. Ghosh, N. Kole. *J. Coord. Chem.*, **65**, 2280 (2012); (h) B. Biswas, A. Al-Hunaiti, M.T. Räisänen, S. Ansalone, M. Leskelä, T. Repo, Y.-T. Chen, H.-L. Tsai, A.D. Naik, A.P. Railliet, Y. Garcia, R. Ghosh, N. Kole. *Eur. J. Inorg. Chem.*, **28**, 4479 (2012).
[13] (a) G.M. Sheldrick. *Acta Crystallogr.*, **64**, 112 (2008); (b) O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann. *J. Appl. Cryst.*, **42**, 339 (2009).
[14] L.J. Farrugia. *J. Appl. Cryst.*, **45**, 849 (2012).
[15] (a) F. Marandi, Z. Nikpey, M. Khosravi, H.-K. Fun, M. Hemamalini. *J. Coord. Chem.*, **64**, 3012 (2011); (b) F. Marandi, A. Morsali. *Inorg. Chim. Acta*, **370**, 526 (2011).
[16] (a) J.R. Lillehaug, K. Kleppe. *Biochemistry*, **14**, 1225 (1975); (b) C. Minero, G. Mariella, V. Maurino, E. Pelizzetti. *Langmuir*, **16**, 2632 (2000); (c) M.C. Lu, J.N. Chen, C.P. Chang. *Chemosphere*, **35**, 2285 (1997).
[17] L. Shimoni-Livny, J.P. Glusker, C.W. Bock. *Inorg. Chem.*, **37**, 1853 (1998) and references therein.
[18] (a) A. Bhunia, E. Zangrando, S. Mistri, S.C. Manna. *Inorg. Chim. Acta*, **409**, 528 (2014); (b) J.G. Sole, L.E. Bausa, D. Jaque. *An Introduction to Optical Spectroscopy of Inorganic Solids*, Wiley, Chichester (2005).