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Synthesis, supramolecular architecture and fluorescence property of a mixed ligand 1D Pb(II) coordination polymer

Prafullya Kumar Mudi, Chanchal Kumar Pal and Bhaskar Biswas

Department of Chemistry, University of North Bengal, Darjeeling, 734013, India
prafullya642@gmail.com (P.K.M.), ckpal2041@gmail.com (C.K.P.), bhaskarbiswas@nbu.ac.in (B.B.)

* *Corresponding author at: Department of Chemistry, University of North Bengal, Darjeeling, 734013, India.*
Tel: +91.0353.2776381 Fax: +91.0353.2776381 e-mail: bhaskarbiswas@nbu.ac.in (B. Biswas).

RESEARCH ARTICLE

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ABSTRACT

A one dimensional (1D) lead(II) coordination polymer, $[Pb(Phen)(NO_3)(OAC)(H_2O)]_n$ (1) (Phen = 1,10-Phenanthroline; OAc = Acetate) was isolated in crystalline phase and characterized through different analytical techniques. Single crystal X-ray structural analysis of compound 1 revealed that the Pb(II) polymer crystallized in a monoclinic system with $P2_1/c$ space group. Pb^{2+} ion adopted a highly distorted octahedral geometry having O3 (water) and O5 (nitrate) at axial positions (∠O3-Pb1-O5 of 145.02°) and acetate oxygen (O4), phenanthroine nitrogens (N3, N4) and oxygen (O2) atom from bridging nitrate made a distorted square plane. This Pb(II) polymer exhibited good fluorescence property in solid state. The steric arrangement of distorted square plane around Pb(II) ion by Phen, acetate and bridging nitrate ion makes a huge gap around Pb(II) ion where a stereo-active lone pair of electrons may possibly be occupied.

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1. Introduction

Heavier metals in the periodic table have a natural tendency to keep the s orbital electrons “inert” and exhibit two units lower oxidation number than the common oxidation number [1]. The relativistic effect accounts on the inertness of the electron pair in 6s orbital which is particularly caused by completely filled 4f subshell in atom. The Pb(IV) species behave as strong oxidising agents in aqueous medium and consequently reduced to Pb(II) species with evolution of oxygen gas in a spontaneous manner. The Pb ions may form a diversified coordination geometry ranging from coordination numbers 2 to 12 and may produce a large variety of coordination geometry [2,3]. The orbital containing a lone pair of electrons may be treated as an additional ligand in the primary zone of coordination which holds more space compared to an ordinary ligand [4,5]. Moreover, molecular orbital theory (MOT) can’t always able to account on the occupation of 6s/6p orbital on Pb(II) ion. Moreover, substantial differences between the energies of the orbitals and their spatial arrangement of the corresponding wave functions may not support this phenomenon [6-8]. Perhaps, the stereo-chemical activity of 6s orbital observed in Pb(II) compounds should be treated as an outcome of an interaction between 6s orbital of Pb(II) ion and np orbital of the ligand that results in structural distortions to energetically minimize these unfavourable covalent interactions [6,8].

Extensive literature survey indicates that Shimoni-Livny *et al.* proposed two general classes of Pb(II) coordination compounds, hemidirected and holodirected [9]. In hemidirected type of Pb(II) complexes, the electronic distribution around the metal centre is irregularly distributed to a greater extent and this is due to the interactions between antibonding metal-ligand orbitals that create a huge gap in the coordination environment. For the latter, very even electronic distributions are observed around the metal centre in the coordination sphere. Ren *et al.* and Morsali *et al.*, previously reported different 1D to 3D Pb(II) coordination polymers having N-donor auxiliary ligands with different topological views [10-12]. Previously, we were able to produce a same class of 1D coordination polymer containing 2,2’-bipyridine, nitrate and water using similar reaction methodology [13].

The growing demand of Pb(II) compounds in industry, like paints and batteries [14] impacts hugely on the environment and induces severe damage on human health. Therefore, the research on production, structural aspects and applicability of Pb(II) compounds in real devices of create a great deal of interest to us [15-20].

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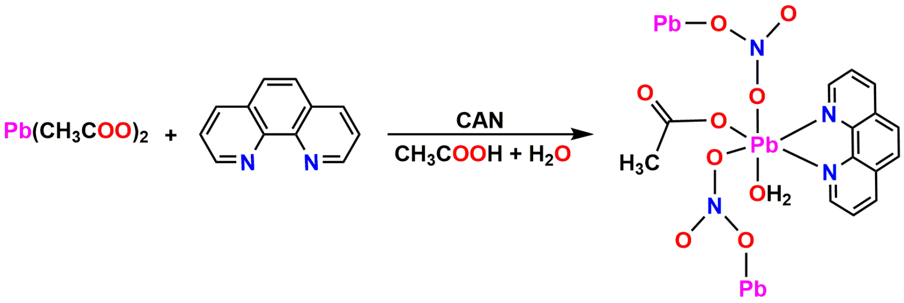

Scheme 1. Synthetic route of Pb(II) polymer (**1**).

In this present work, we have prepared a 1D lead(II) coordination polymer consisting of phenanthroline, acetate, nitrate ion and water as ancillary ligands. The physicochemical and structural properties of this Pb(II) compound have been studied through different analytical techniques. Computational modelling on X-ray structure displays very close structural relationship and strongly recommends the formation of 1D octahedral Pb(II) structure in solid state.

2. Experimental

2.1. Preparation of the complex

2.1.1. Chemicals, solvents and starting materials

High purity 1,10-phenanthroline (Lancaster, UK), ammonium ceric nitrates (Aldrich, UK), and lead acetate (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)

1,10-Phenanthroline (0.180 g, 1 mM) in 10 mL 60:40 (*v*:*v*) AcOH:H_2O solution was added drop wise to a solution of $Pb(CH_3COO)_2$ (0.325 g, 1 mM) in the same solvent (10 mL) and kept on a magnetic stirrer for 30 minutes with slow stirring. The total reaction solution was remained colourless. Solid ceric ammonium nitrate (0.550 g, 1 mM) was added to above solution portion wise and continued string for another 20 mins. The colourless solution was filtered and the supernatant liquid was kept in air for slow evaporation. After 15-20 days, the colourless single crystals were separated out. The crystals were washed with hexane and dried in vacuum over silica gel indicator. *Polymer* ***1***: Yield: 0.258 g (~79% based on metal salt). Anal. calcd. for $C_{14}H_{13}N_3O_6Pb$ (**1**): C, 31.94; H, 2.49; N, 7.98. Found: C, 31.89; H, 2.58; N, 7.91. IR (KBr, ν, cm^{-1}): 3474, 1621, 1589 (C=N), 1384 (NO_3). UV-Vis (λ_{max}, nm): 237, 258-282.

2.2. Physical measurements

Infrared spectrum (KBr) was recorded with a FTIR-8400S Shimadzu spectrophotometer in the range 400-3600 cm^{-1}. Solid state UV-Vis analysis was recorded on an Agilent Cary 5000 UV1204M050 Spectrometer. Steady state fluorescence was measure with Hitachi F-7000 spectrofluorometer in solid state. Elemental analyses were performed on a Perkin Elmer 2400 CHN Elemental Analyzer.

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 Mercury375R (2×2 bin mode) CCD detector. The data were collected with graphite monochromated MoKα radiation (λ = 0.71075 Å) at 293(2) K using ω scans. The data were reduced using Crystal Clear suite [21] and the space group determination was done using OLEX2. The structure was resolved by direct method and refined by full-matrix least-squares procedures using the SHELXL-97 software package [22] using OLEX2 suite [23].

3. Results and discussion

3.1. Syntheses and formulation

One dimensional Pb(II) polymer was prepared by addition of Pb(II) acetate to 1,10-phenanthroline ligand followed by ceric ammonium nitrate (CAN) in aqueous acetic acid medium. CAN provided the supply of nitrate ion in the reaction medium which acted as a bridging unit to adjacent Pb(II) ion and help to form this 1D Pb(II) polymer. We used lead nitrate instead of lead acetate in absence of CAN under similar reaction condition to prepare this polymer but unfortunately, we were not able to produce the Pb(II) polymer. Addition of CAN is a mandatory step of the synthetic procedure for the successful production of Pb(II) polymer. To synthesis the polymer, the coordination geometry of Pb(II) ion in this coordination polymer was defined principally with single crystal X-ray diffraction study in support with different spectroscopic and analytical techniques. The suitable colourless crystals were obtained from the reaction mixture with slow evaporation technique. The structural formulation was confirmed by elemental analysis, IR, UV-Vis, and X-ray structural analysis of the Pb(II) polymer. The schematic presentation of synthesis is given in Scheme 1.

3.2. Description of crystal structure and supramolecular interactions

The X-ray structural analysis of compound **1** reveals that Pb(II) compound exists as a 1D coordination polymer in monoclinic system with $P2_1/c$ space group. An ORTEP diagram of the asymmetric unit of the Pb(II) complex with an atom labelling scheme is shown in Figure 1. The crystallographic and structural refinement parameters for compound **1** are given in Table 1. The crystallographic metal centric bond angles and distances are presented in Table 2. In each of the asymmetric monomeric units in the polymeric $[Pb(phen)(NO_3)(H_2O)(OAc)]_n$ structure, Pb(II) ion is chelated through two nitrogen atoms of Phen ligand with Pb(II)-N distances of 2.552 and 2.488 Å and acetate oxygen (O5), and oxygen (O3) atom of bridging nitrate to complete square plane of the octahedral geometry.

The oxygen atoms, O1 from water and O2 from nitrate ions coordinate from the axial positions with a distorted bond angle, ∠O1-Pb1-O2 as 144.97° (Table 2).

Table 1. Crystallographic data of $[Pb(Phen)(NO_3)(OAC)(H_2O)]_n$ (**1**).

Parameters	**Compound 1**
CCDC Number	1900187
Empirical	$C_{28}H_{26}N_6O_{12}Pb_2$
Formula weight	1052.93
Temperature (K)	100
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	7.1786(6)
b (Å)	9.9706(7)
c (Å)	21.0908(16)
Volume (Å^3)	1488.9(2)
Z	2
ρ (g.cm^{-3})	2.349
μ (mm^{-1})	11.356
F (000)	992
Index ranges	$-9 \le h \le 9$
	$-12 \le k \le 11$
	$-27 \le l \le 27$
θ ranges (°)	3.2-27.5
Total reflections	12844
Unique reflections	3323
R_1 [I > 2σ(I)]	0.0323
R_{int}	0.041
wR_2 (all data)	0.0811
GooF	1.03
Largest peak and hole (eÅ^{-3})	-1.85, 1.43

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

Bond distances			
Pb1-O1	2.458(4)	Pb1-O5	2.704(5)
Pb1-O2	2.740(4)	Pb1-N2	2.488(5)
Pb1-O3	2.971(4)	Pb1-N3	2.552(4)
Bond angles			
O1-Pb1-O2	144.97(13)	O5-Pb1-O6	44.0(15)
O1-Pb1-O3	147.95(13)	O5-Pb1-N2	80.16(15)
O1-Pb1-O5	80.48(14)	O5-Pb1-N3	138.93(14)
O1-Pb1-O6	108.43(15)	O3*-Pb1-O5	130.58(15)
O1-Pb1-N2	82.81(14)	O6-Pb1-N2	116.52(15)
O1-Pb1-N3	73.32(14)	O6-Pb1-N3	177.07(15)
O1-Pb1-O3*	82.70(14)	O6-Pb1-O3*	100.71(14)
O2-Pb1-O3	43.89(13)	N2-Pb1-N3	65.82(15)
O2-Pb1-O5	123.63(15)	O3*-Pb1-N2	142.65(13)
O2-Pb1-O6	106.29(14)	O3*-Pb1-N3	77.08(14)
O2-Pb1-N2	77.76(14)	O3-Pb1-N2	69.11(13)
O2-Pb1-N3	72.19(13)	O3-Pb1-N3	106.90(13)
O2-Pb1-O3*	95.40(15)	O3-Pb1-O3*	129.13(13)
O3-Pb1-O5	79.80(15)	O3-Pb1-O6	72.94(14)

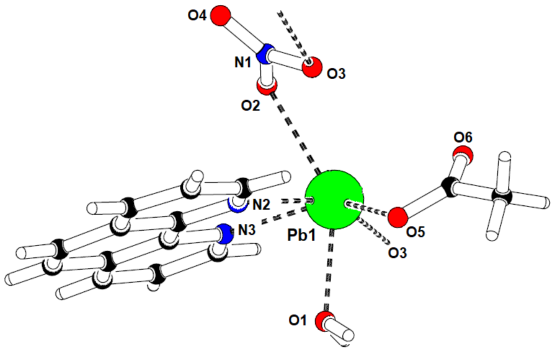

Figure 1. ORTEP diagram of asymmetric unit in $[Pb(Phen)(NO_3)(OAc)(H_2O)]_n$ (**1**) (30% ellipsoid probability) with atom numbering scheme.

The primary zone of coordination for Pb(II) ions in this coordination polymer consists of six coordination site. The Pb(II) monomers are interconnected with adjacent monomeric units through bridging nitrate oxygen atom and produce polymeric unit in the crystalline solid state. The distances between adjacent Pb(II) ions in the polymeric units are 5.540 Å. Close inspection on the arrangement of the Phen ligand, acetate ion and bridging nitrate ion in the square planar geometry of the polymeric structure strongly suggests about a highly distorted square plane and indicates that a huge space gap in the square planar geometry around Pb(II) ion, [∠O(3)-Pb-O(5) = 130.58°] occupies probably a stereo-active s-orbital lone pair of electrons. The observed reduction of the Pb(II)-N bond opposite to lone pair (2.488 Å) compared to adjacent crystallographic bond length, Pb(II)-N, 2.552 Å consolidates the existence of stereo-active lone pair around Pb(II) ion [24-28].

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

D–H···A (Å)	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠D–H···A (°)	Symmetry
C(1)-H(1A)...O3	0.95	2.40	3.157	136	-x, -1/2+y, 1/2-z
C(3)-H(3)...O6	0.95	2.51	3.268	137	*x*, 1/2-*y*, 1/2+*z*
C(8)-H(8)...O5	0.95	2.58	3.235	126	-
O(1)-H(1A)...O5	0.88	2.15	2.977	156	1-*x*, -1/2+*y*, 1/2-*z*

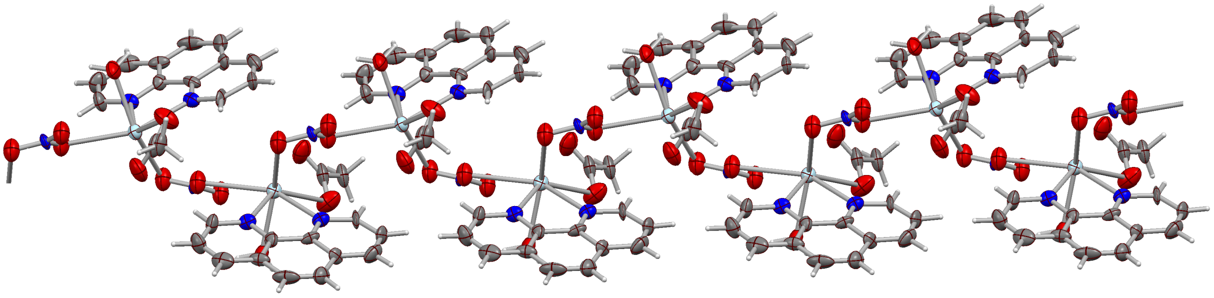

Figure 2. Formation of 1D polymer $[Pb(Phen)(NO_3)(OAc)(H_2O)]_n$ (**1**) along the crystallographic *b* axis.

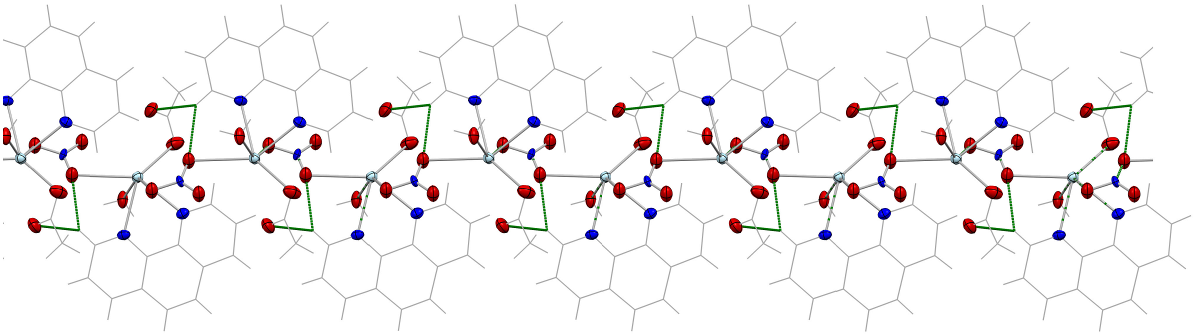

Figure 3. Acetate and nitrate mediated 1D H-bonded network of Pb(II) polymer along the crystallographic *b* axis. C-H···O interactions are seen in green dotted interaction in this wireframe model.

Nitrate ions in this 1D polymeric $[Pb(phen)(NO_3)(H_2O)(OAc)]_n$ compound play pivotal role in the construction of the coordination Pb(II) polymer. One oxygen atom (O2) of the nitrate ion makes a coordinate bond with Pb(II) ion, Pb(1)-O(2) = 2.74 Å while another oxygen atom (O3) of the same nitrate ion bridges with an adjacent Pb(II) ion, Pb(1)-O(3) = 2.833 Å to extend the monomeric unit to polymeric one. Both the nitrate and acetate ions coordinate with Pb(II) ion in a monodentate fashion and coordination distances between Pb-O2 and Pb-O5 bonds remain very close to each other. However, O-atom (O1) from aqua molecule forms a strong coordination with Pb(II) ion (Pb(1)-O(1) = 2.457 Å). The presence and the activity of stereo-chemical lone pair around Pb(II) centre in Pb(II) coordination compounds has been previously discussed by Shimoni-Livny *et al.* in a meticulous review of crystal data available in the Cambridge Structural Database (CSD) [29]. They classified the coordination geometry around Pb(II) centres as holodirected, in which the coordinated donor atoms from ligand are directed throughout the surface of an encompassing sphere, although hemidirected nature of coordination refers to the coordination by the donor centres of ligand those are directed partly of the coordination environment, leaving a gap in the distribution of bonds to the ligand. For our Pb(II) crystal structure, stereo active lone pair enforces to uneven coordination around the lead atoms leading to hemidirected coordination geometry containing a significant gap *trans* to the chelated phenanthroline ligand (Figure 2).

Examining the effect of supramolecular weak forces in the construction of long range crystalline architectures for Pb(II) polymer, it is revealed that H-bonding interactions remain the primary responsible factor in providing additional stabilization to the 1D Pb(II) coordination polymer. Intermolecular hydrogen bonding like O–H···O and C–H···O are functioning in the formation of long range crystalline architecture ranging from 2.25 to 2.55 Å, which is an indication of very strong to strong type hydrogen bonding interactions. The 1D chain grows along *b* axis mediated through C–H/OH···O hydrogen bonds [C(1)-H(1)···O3, 2.40 Å; C(3)-H(3)···O6, 2.51 Å, C(8)-H(8)···O5, 2.58 Å, O(1)-H(1A)···O5, 2.15 Å; Figure 3, Table 3].

3.3. Fluorescence properties of the Pb(II) polymer in solid state

The fluorescent properties of the 1D Pb(II) polymer (λ_{ex} = 267 nm) was recorded in solid state is presented in Figure 4. The emission wavelength of Pb(II) polymer at solid state was found as 370 nm (Figure 4). Ligand-to-metal charge transfer (LMCT) may account on this nature of emission [30-35]. Previous scientific literature on the Pb(II) polymers also agree with our observation [13].

4. Conclusions

In this work, we present the synthetic approach, structural characterization and fluorescence properties of a mixed ligand Pb(II) coordination polymer, $[Pb(Phen)(NO_3)(H_2O)(OAc)]_n$. The primary zone of coordination for Pb(II) ion is unusually diverse for having the involvement of antibonding molecular orbital interactions between 6s orbital of Pb(II) ion and np

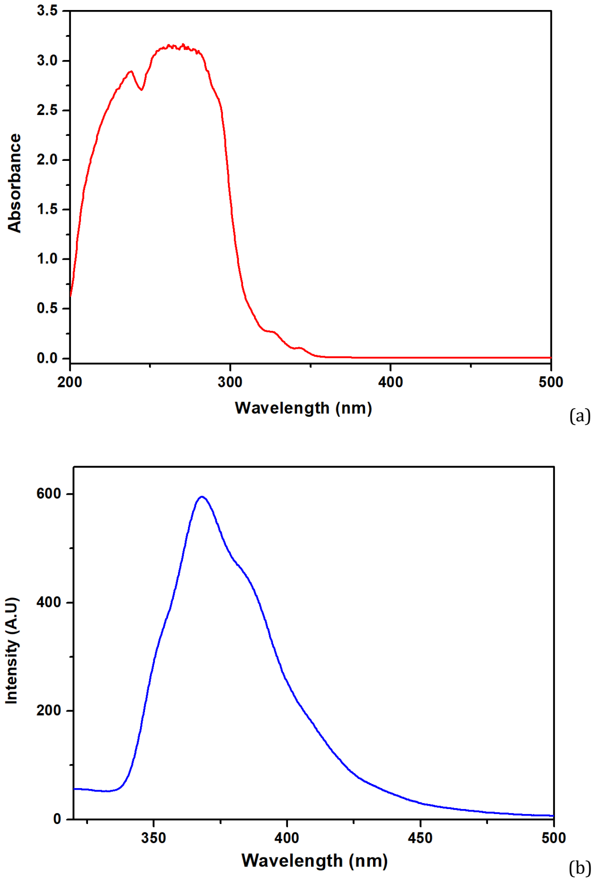

Figure 4. Solid state absorbance spectrum of compound **1** (a) and solid state fluorescence spectrum (λ_{ex} = 267 nm) for compound **1** (b).

orbital of phenanthroline in causing unsymmetric electron distribution at Pb(II) centre. This driving force accounts on the formation of hemidirected Pb(II) complexes. Solid state fluorescence measurements for this lead(II) polymer exhibits good luminescent property of the mixed ligand Pb(II) polymer. More interestingly, there are few examples available in scientific literatures where acetate and nitrate ions are behaving as monodentate coordinating system and from this perspective, the successful preparation of compound **1** will definitely enrich the molecular library of lead complexes.

Supporting information

CCDC-1900187 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/ , or by e-mailing data_request@ccdc.cam.ac.uk , or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

ORCID

Prafullya Kumar Mudi
http://orcid.org/0000-0002-3365-0961
Chanchal Kumar Pal
http://orcid.org/0000-0003-2821-8880
Bhaskar Biswas
http://orcid.org/0000-0002-5447-9729

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