3D purely inorganic lead-azide coordination polymer constructed by exclusive *end-to-end* azido binding

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ARTICLE INFO

ABSTRACT

One pot synthesis of a purely inorganic framework of azido-lead(II) complex with molecular formula $[Pb_3(N_3)_6]_n$ has been made by using 5-aminotetrazole (5-ATZ) ligand as starting material. X-ray single crystal structure determination revealed the presence of two types of Pb-centers (Pb1 and Pb2). One-dimensional propagation of Pb1 centers with azide segment gives an infinite zig–zag 1D chain along *c*-axis. 2D sheet is formed along *bc*- and *ac*-plane with the 1D chain. It is interesting to identify another infinite 1D chain along *a*-axis by connecting Pb2 centers via azide linkage. The compound displays an overall 3D structure. All the connectivity of azide in complex **1** show exclusive end-to-end (*i.e.*, μ-1,3) binding.

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1. Introduction

Solid energetic materials are very important because of their technological application as explosives and fuels. Heavy metal azides are generally unstable in nature. Lead, cupric and mercuric azides are very sensitive and powerful solid explosives which are used as detonants. These azides can explode and detonate in solid state when they are exposed to suitable external stimulus like heat, impact, friction or electric discharge [1–6]. Although, variety of polynuclear metal azide complexes have been reported with various organic co-ligands where the structural and electronic versatility of the azide linker is applied to explore the properties like magnetism, liquid crystal behavior, photo-device activity and catalysis [7], however, no example of purely inorganic polynuclear metal-azido compound of lead, copper or mercury is present in the literature. Lead(II) center offers a large variety of coordination numbers (2–10) due to the presence of its 6 s electron pair with considerably large ionic radius. This flexibility in coordination number influences the construction of two discrete structural categories named as hemidirected (bond to ligand donor centers are directed to one part of the circling globe) and holodirected (bonds to the ligand donor centers are directed throughout the surrounding globe) coordination (Fig. 1) [8].

Few zinc azide complexes with various pyridine derivatives such as 4-methyl pyrimidine, 2-picoline-*N*-oxide, pyridine, 3-picoline-*N*-oxides and amino-pyrazine are reported in literature emphasizing on structures of higher dimensionality, which reveals that the binding mode of the azide ligand plays an important role [9] to express various functional behavior. Carranza et al. described the structure and magnetic properties of copper azido complex involving an symmetric single end-on azido bridge [10]. Recently Mautner et al. reported 1D Mn-azide systems with 2-aminopyridine and 4-azidopyridine having both end-on and end-to-end binding mode of the azide [11]. In a recent report, it has been observed that the magnetic behavior of Mn-azide complexes owes to the bridging behavior of azide ligand [12]. Mukherjee et al. recently reported some transition metal-azido extended complexes with various anionic and neutral co-ligands that show distinct magnetic behavior [13]. Hence, it is evident that azide ion is an extremely potential ligand which can bridge the metal centers either in the end-on (μ-1,1) or end-to-end (μ-1,3) modes and simultaneously produces huge number of topologies for higher dimensional complexes; all such possibilities are structurally characterized for transition metal complexes [14–16].

From a desire to synthesize an exclusive azido-lead(II) coordination polymer we tried all conventional routes of synthesis but it did not worked. Finally we attempted the hydrothermal reaction by reacting the metal salt with 5-aminotetrazole by exploiting the idea of in situ decomposition of 5-aminotetrazole to azide which has been studied earlier by Brady [17]. Brady investigated the elec-

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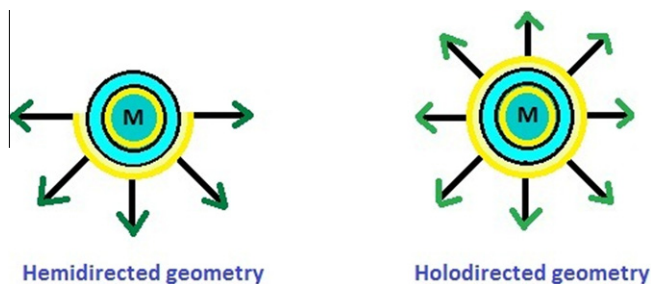 *E-mail addresses:* sudipta@mail.vidyasagar.ac.in, icsd2@yahoo.com (S. Dalai).

Fig. 1. Hemidirected and holodirected coordination around metal center.

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

Empirical formula	Pb_3N_{18}
Formula weight	873.75
Temperature (K)	110(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P n m a
a (Å)	6.6132(2)
b (Å)	16.2733(4)
c (Å)	11.2010(3)
Volume (Å^3)	1205.44(6)
Z	4
$D_{calc.}$ (g m^{-3})	4.815
Absorption coefficient (mm^{-1})	41.828
$F(0\,0\,0)$	1488
θ_{max} (°)	26.38
Reflections collected/unique	4003/1233
Data $I > 2\sigma(I)$	1129
Parameters	104
Goodness-of-fit on F^2	1.129
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0411$, $wR2 = 0.1072$
R indices (all data)	$R1 = 0.0457$, $wR2 = 0.1098$
Largest diff. peak and hole (e Å^3)	0.456, −0.201

Table 2
Stretching frequencies of different coordination complexes with azido ligands in the literature.

Coordination complex	Reference	$v_{as}(N+3^-)$ in cm^{-1}	$v_s(N+3^-)$ in cm^{-1}
Zinc-azide complex	[9]	2099, 2072	1291, 1323
Copper-azide complex	[10]	2084, 2035	1292, 1333
Manganese-azide complex	[11]	2107, 2082	1289, 1334
Cobalt-azide complex	[28]	2089, 2050	1280, 1338
Gold-azide complex	[29]	2034, 2030	1251, 1261
Paladium-azide complex	[28]	2056, 2037	1253, 1262
Platinum-azide complex	[28]	2028, 2022	1253, 1275

synthesize an exclusive inorganic coordination polymer of azido-lead(II), $[Pb_3(N_3)_6]_n$. The compound is characterized by IR study and X-ray single crystal structure analysis.

2. Experimental

2.1. Materials

All the chemicals for the syntheses were used as received. Lead nitrate was obtained from MERCK. 5-Aminotetrazole was purchased from SIGMA–ALDRICH Inc.

2.2. Physical measurements

IR spectrum for **1** was recorded in a JASCO FT/IR-6200 using the ATR technique in the range 4000–400 cm^{-1}. Elemental analyses (C, H, N) were performed using a Perkin–Elmer 240C elemental analyzer.

2.3. Synthesis of $[Pb_3(N_3)_6]_n$ (**1**)

An aqueous solution (10 mL) containing $Pb(NO_3)_2$ (0.5 mmol, 0.1656 g) and 5-aminotetrazole (1 mmol, 0.085 g) was placed in a Parr Teflon-lined stainless steel vessel (25 mL) under autogenous pressure, which was heated to 160 °C for 3 days and subsequently cooled to room temperature. The colorless transparent solution is collected in 100 mL beaker and kept in the desiccators for slow
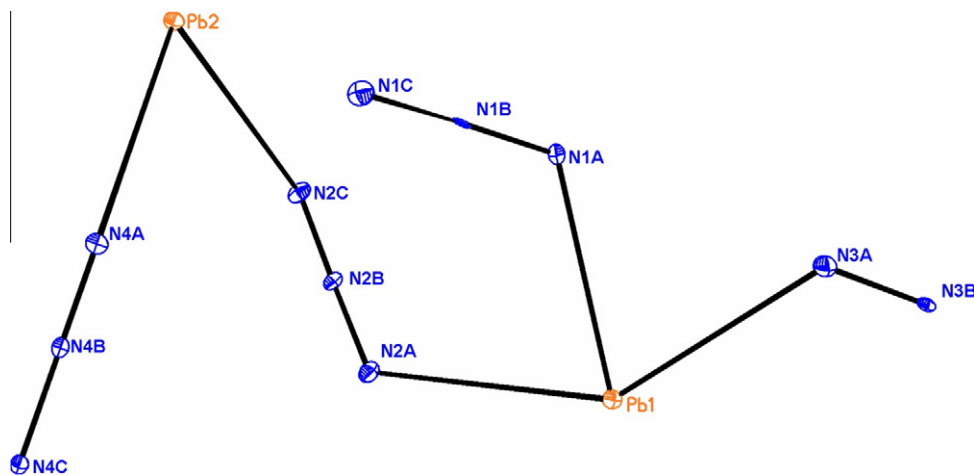
tron impact-induced fragmentation of 5-ATZ and recommended the formation of hydrogen azide (HN$_3$) during the decomposition of 5-ATZ. Several other experimental reports [18–23] also concluded the formation of hydrogen azide as product during the thermal decomposition of 5-ATZ. Inspired by all these facts we reacted 5-ATZ with $Pb(NO_3)_2$ hydrothermally and had been successful to

Fig. 2. Asymmetric unit of complex **1**.
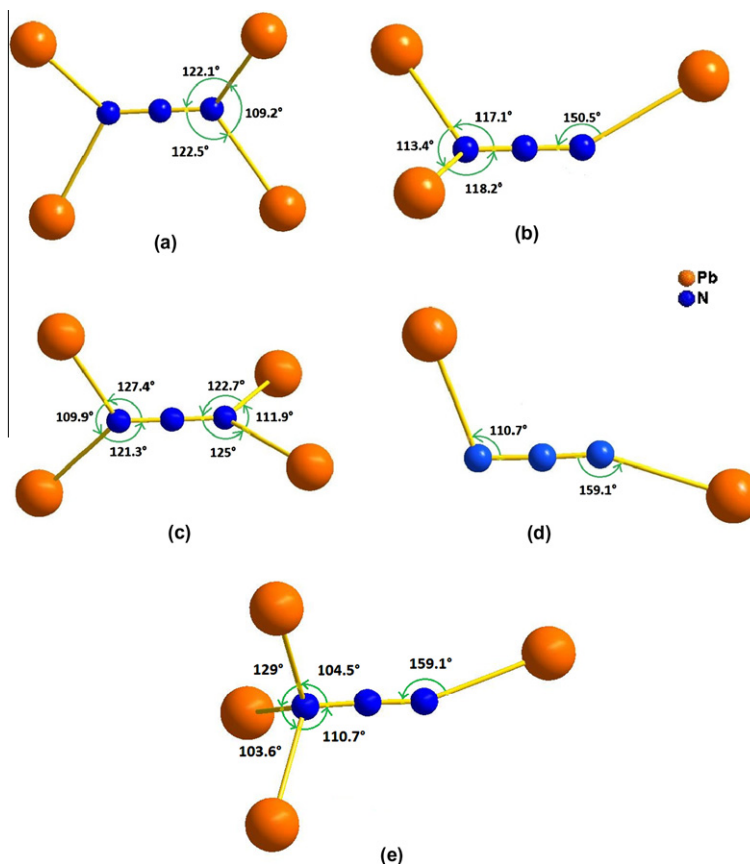
Fig. 3. End-to-end (μ-1,3) binding modes of azido ligand present in complex **1**.

evaporation. Colorless block shaped single crystals were obtained from solution after 3 days. The single crystals were isolated by decanting the supernatant liquid and washed with deionized water, ethanol and dried in air. Yield 56%. Anal calcd. for Pb_3N_{18} (%): N, 28.85. Found: 28.83%. IR (v/cm^{-1}): 2100, 2030, 2015, 1360, 1329, 1321, 1041, 842, 811.

2.4. X-ray structure analysis

The data collection for the structures reported was carried out with an Oxford Diffraction Gemini diffractometer equipped with a Mo Kα radiation ($\lambda = 0.71073$ Å) source ω scan mode at 110 K. Data were processed using the *CrysAlis-CCD* programs [24]. The structure was determined by direct methods procedures in *SHELXS* [25] and refined by full-matrix least-squares methods, on F^2's, in *SHELXL* [25]. The crystallographic data and the refinement results are listed in Table 1.

3. Results and discussion

The FT-IR spectrum of **1** displays strong band $\sim$2030 cm^{-1}, [$v_{as}(N_3^-)$]. The other related bands $\sim$1327 (s) and $\sim$1160 (w) cm^{-1} is due to $v_s(N_3^-)$ mode confirming the asymmetry of the azido bridging ligands [26,27]. The stretching frequencies of the coordination complexes with azide ligand reported in the literature are given in Table 2 clearly indicate that the highest frequency band of $v_{as}(N_3^-)$ is due to *end-on* binding (i.e., μ-1,1-) and the lowest frequency band is for the *end-to-end* binding of the azido ligand (i.e., μ-1,3). So it is quite obvious that in complex **1** strong IR band $\sim$2030 cm^{-1} indicative of *end-to-end* (μ-1,3) N_3^- binding which is further confirmed from X-ray single crystal structure analysis.

Table 3
Bond lengths (Å), bond angles around central Pb(II) ions in **1**.

Pb1	N2A		2.694(8)
Pb1	N1A		2.619(9)
Pb1	N3A		2.602(0)
Pb1	N2A[i]		2.799(9)
Pb1	N2C[ii]		2.701(10)
Pb1	N3A[iii]		2.756(0)
Pb1	N1A[iii]		2.604(9)
Pb1	N4C[iv]		2.897(5)
Pb2	N4A		2.672(3)
Pb2	N1C		2.896(10)
Pb2	N2C		2.567(8)
Pb2	N1C[v]		2.837(10)
Pb2	N2C[vi]		2.567(8)
Pb2	N1C[vi]		2.896(10)
Pb2	N1C[vii]		2.837(10)
Pb2	N4C[viii]		2.588(2)
N2A	Pb1	N1A	73.97(3)
N1A	Pb1	N2C[ii]	76.90(3)
N2C[ii]	Pb1	N3A	78.91(3)
N3A	Pb1	N4C[i]	79.57(2)
N4C[i]	Pb1	N3A[iii]	69.69(2)
N3A[iii]	Pb1	N2A[i]	70.15(3)
N2A[i]	Pb1	N1A[iii]	73.84(3)
N1A[iii]	Pb1	N2A	82.97(3)
N4C[viii]	Pb2	N1C[vii]	70.93(2)
N1C[vii]	Pb2	N2C[vi]	78.01(3)
N2C[vi]	Pb2	N1C[vi]	77.41(3)
N1C[vi]	Pb2	N4A	68.89(2)
N4A	Pb2	N1C	68.89(2)
N1C	Pb2	N2C	77.41(3)
N2C	Pb2	N1C[v]	78.01(3)
N1C[v]	Pb2	N4C[viii]	70.93(2)

Symmetry codes: i = $1 - x$, $1 - y$, $-z$; ii = $-x$, $1 - y$, $-z$; iii = $0.5 + x$, y, $0.5 - z$; iv = $1 - x$, $0.5 + y$, $-z$; v = $-0.5 + x$, y, $0.5 - z$; vi = x, $0.5 - y$, z; vii = $-0.5 + x$, $0.5 - y$, $0.5 - z$; viii = $-1 + x$, y, z.
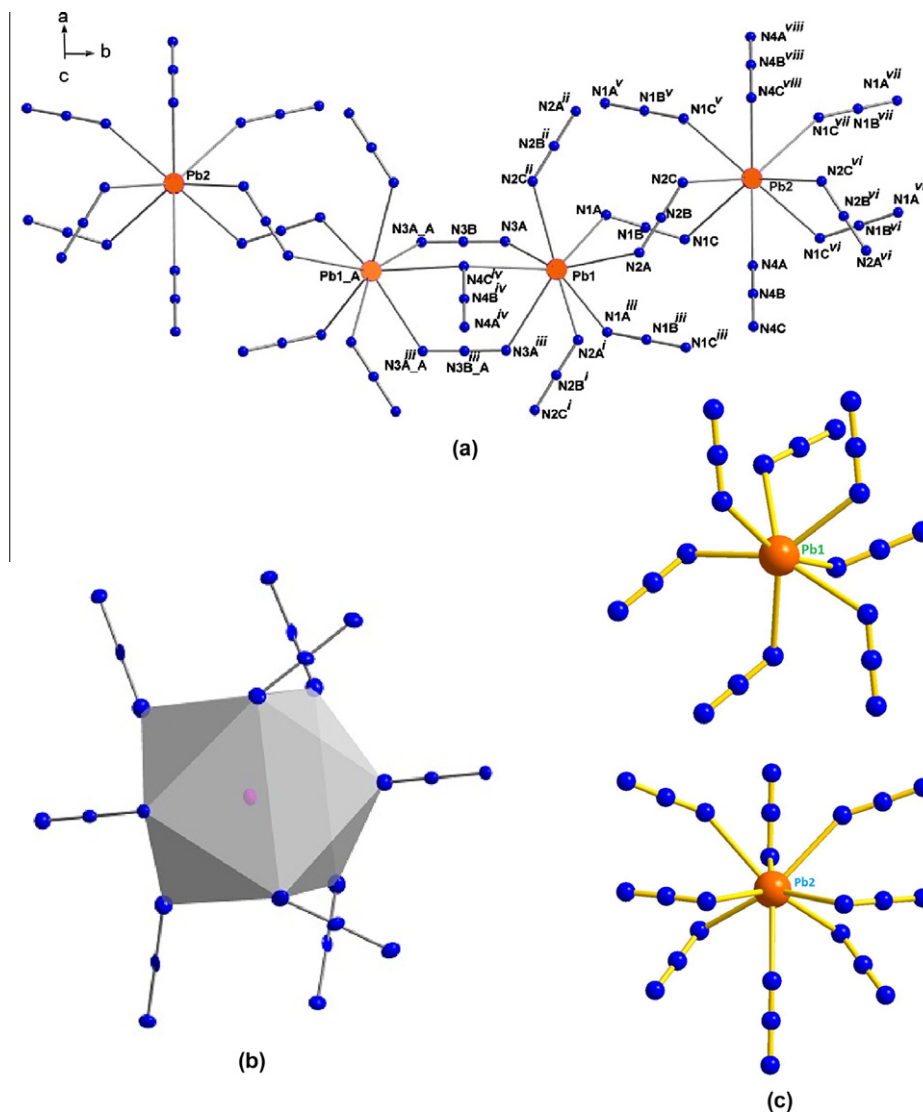
Fig. 4. (a) Coordination environment of complex **1** and geometry around Pb(II) centers; (b) octa-coordinated Pb(II) centers displaying distorted capped prism geometry; (c) holodirected geometry around Pb1 and Pb2 centers.

The single-crystal X-ray analysis of **1** revealed that there are two crystallographic independent Pb(II) centers (Pb1 and Pb2) in the asymmetric units of the structure with different coordination environments as shown in Fig. 2; where both Pb(II) ions bridged by an azide binding through its both ends while each Pb(II) centers are separately attached to one independent azide anion. It is worth nothing that in this complex the azide ligand is coordinated to Pb-center only by end-to-end binding mode and five different kinds of N_3^- coordination is explored (Fig. 3). The Pb1 center of each asymmetric unit are bridged through an azide with 0.5 occupancy of central N(azide) atom. The non-bonded distance between both the Pb(II) ions (Pb1···Pb2) is found to be 6.109(10) Å. Both the Pb(II) ions have an octa-coordinated environment around them. The bond lengths of Pb1–N1A, Pb1–N2A, Pb1–N3A, Pb1–N2C[ii], Pb1–N3A[iii], Pb1–N2A[i], Pb1–N1A[iii], Pb1–N4C[iv] are found to be in the 2.602–2.897 Å range. Similarly, Pb2 coordinates to N4A, N1C, N2C, N1C[v], N2C[vi], N1C[vi], N1C[vii] and N4C[viii] atoms with bond distances in the 2.567(8)–2.897(0) Å range. The bond distances are in normal Pb–N bond distance range and comparable with those observed in literature [30]. The longer bond distances (>2.8 Å) indi-

cates a weak interaction of these N-atoms with the metal. The bond length and bond angle around the central Pb(II) ion is given in Table 3.

The coordination geometry around both the Pb(II) ions (Fig. 4) can be described as a distorted capped prism, with the two faces of the prism are capped. For Pb1 coordination, N3A[iii] caps the N3A–N4C[i]–N2A[i]–N1A[iii] face of the prism while N1A caps its N2C[ii]–N3A–N1A[iii]–N2A face. Similarly for Pb2 coordination, N4A caps N1C[vi]–N2C[vi]–N2C–N1C face of the prism while N4C[viii] caps N2C[vi]–N2C–N1C[v]–N1C[vii] face of the prism. The disposition of azide ligands around the lead displays holodirected geometry [8] where the bonds to ligand atoms are disseminated throughout the face of an encompassing globe. It is very interesting to observe the formation of infinite 1D zig–zag chain along c-axis where two Pb1 atoms are bridged by two different azido groups in μ_2-fashion forming distorted squares (Fig. 5a) having two alternate Pb···Pb distances of 4.366(5) and 4.552(5) Å along the chain. Another one-dimensional infinite chain is identified along a-axis by connecting Pb2 centers with two unlike Pb···Pb distances of 4.169(8) and 6.613(9) Å (Fig. 5b). The 1D chains (formed by Pb1) are further con-
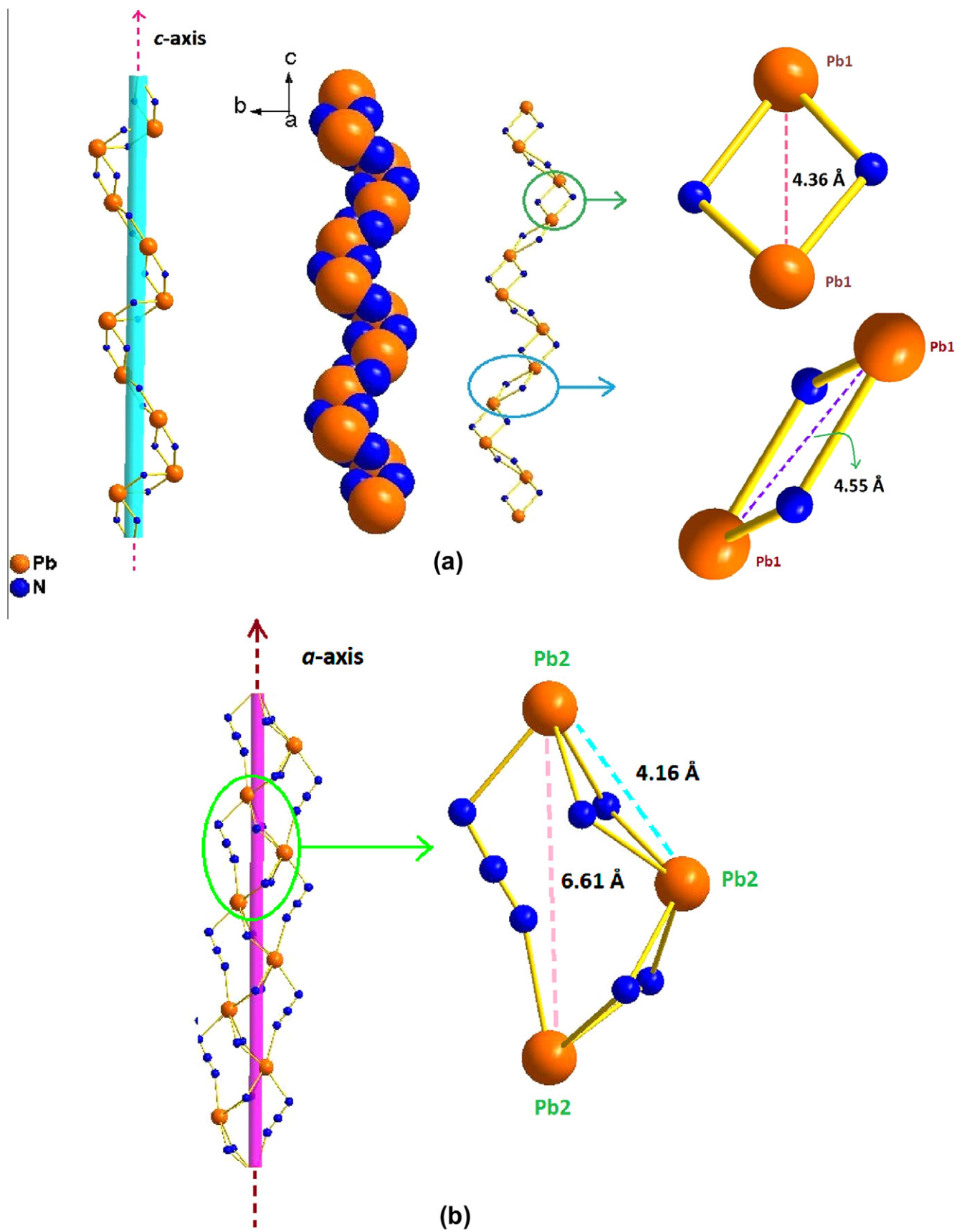
Fig. 5. Infinite 1D zig–zag chain of (a) Pb1 along *c*-axis and (b) Pb2 along *a*-axis.
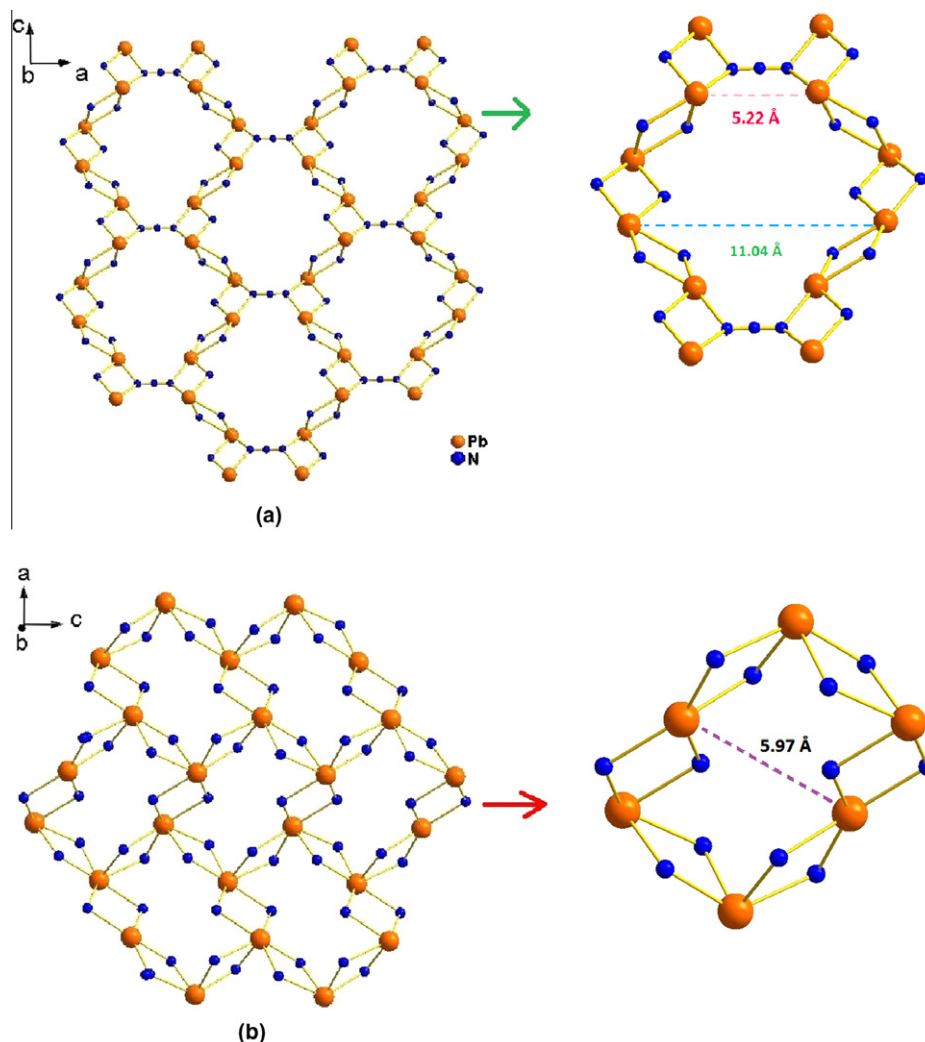
Fig. 6. Formation of 2D sheet with Pb1 along *bc*- (a) and *ac*-plane (b).

nected by azido ligand via $\mu_4 - \eta^2 : \eta^2$ coordination mode (Fig. 3a) through *b*- and *a*-axis respectively leading to the formation of two different 2D sheets in *bc*- and *ac*-plane (Fig. 6) The Pb⋯Pb distances between two adjacent Pb1 centers in the 2D sheet along *bc*-plane are of 5.228(5) Å and 11.044(5) Å, however this distance is 5.977(5) Å in the 2D layer of the *ac*-plane. The azido ligand connects both the 2D layers with the 1D chain (formed by Pb2) via two different binding modes (Fig. 3c and e) to form a 3D network (Fig. 7).

4. Conclusion

In this paper we have synthesized and characterized an azido-lead(II) coordination polymer of formula $[Pb_3(N_3)_6]_n$. This work represents a unique example of the construction of a metal inorganic framework of lead azide by hydrothermal reaction via in situ formation of azide from 5-aminotetrazole and azide ligand in the network is bound to lead(II) via end-to-end binding mode only. Single-crystal X-ray structural analysis revealed 3D geometry of the network with two crystallographically independent lead(II) environments. It is interesting to note that Pb1 atoms with azide fragment grow one dimensionally through *c*-axis to form zig–zag infinite chain. Another infinite 1D chain is developed along *a*-axis

by connecting Pb2 centers. Two different kinds of 2D sheets are formed with Pb1 centers in the *ac*- and *bc*-plane. Finally a 3D structure is evolved when two 2D sheets are connected to the 1D chain (along *a*-axis). In the whole structure the positioning of the azide ligands around Pb(II) centers happened in such a way that the bonds to the ligand atoms are dispersed all the way through the encircling globe leading to holodirected geometry around the lead centers. Construction of lead-azide coordination polymer in this route is the first report of its own kind. This compound is likely to be highly energetic and can be used as explosives and detonants by the use of external stimuli. We are currently extending this work with other metal ions.

Appendix A. Supplementary material

CSD 421895 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge from Fachinfor-
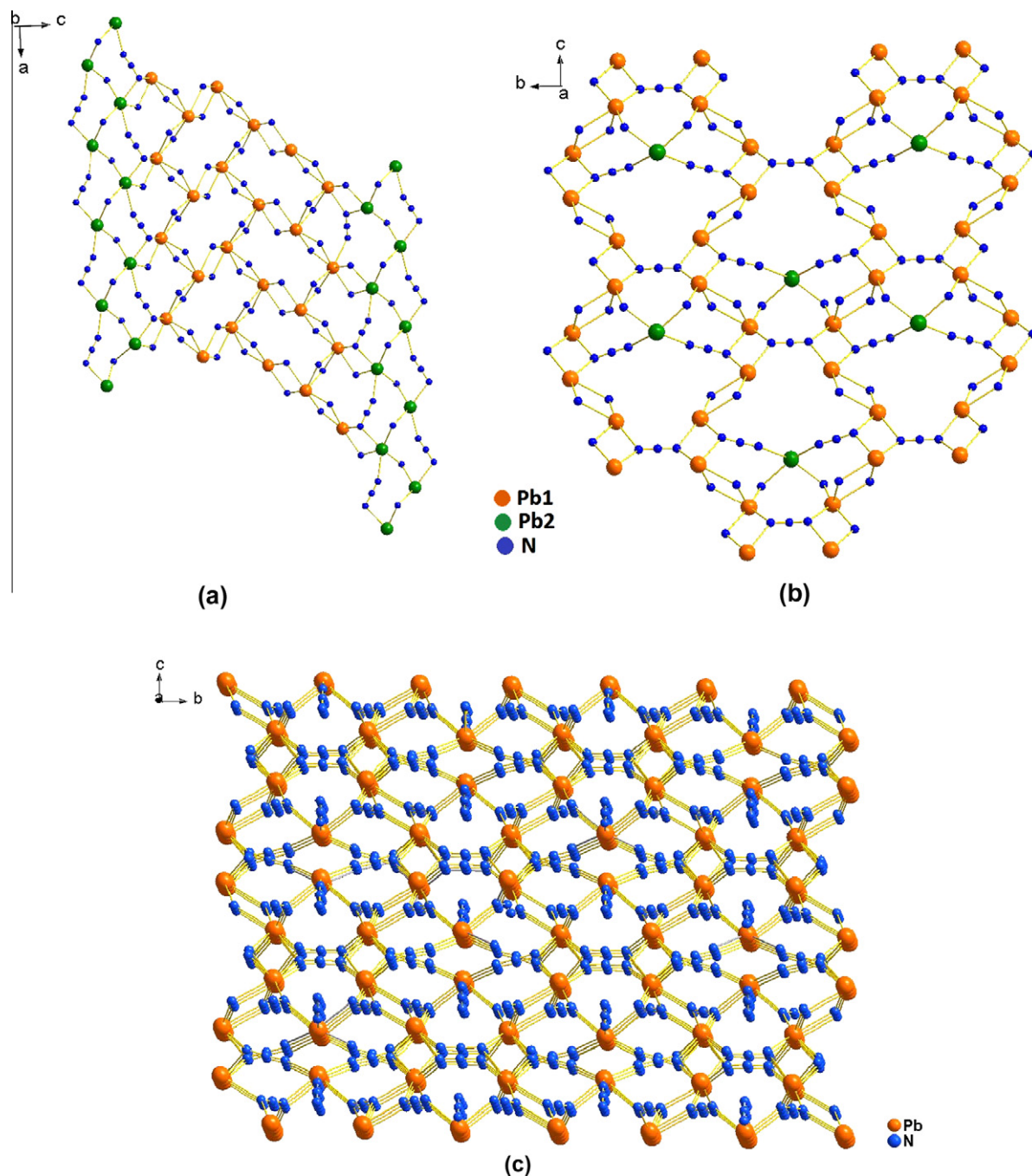
Fig. 7. (a) Connectivity of the 2D sheet (formed by Pb1 centers in *ac*-plane) with 1D chain formed by Pb2 centers (along *a*-axis); (b) connectivity of the 2D sheet (formed by Pb1 centers in *bc*-plane) with 1D chain formed by Pb2 centers (along *a*-axis); (c) the overall 3D structure of complex **1**.

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