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Structural, spectral and theoretical aspects in the coordination of a triazine-based ligand toward lead(II) with a *holodirected* environment

Farzin Marandi^a*, Keyvan Moeini^a, Bahman Mostafazadeh^a, and Harald Krautscheid^b

^a Chemistry Department, Payame Noor University, 19395-4697 Tehran, I. R. Iran

^b Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, D-04103

Leipzig, Germany

Corresponding author (*)

Farzin Marandi E-mail: f.marandi@gmail.com Fax: +98 44 32768825

ABSTRACT

Four complexes, $[Cl(PPTA)_2Pb(\mu-Cl)_2Pb(PPTA)_2Cl]$ (1). $[Br(PPTA)_2Pb(\mu-Br)_2Pb(PPTA)_2Br]$ $[I(PPTA)_2Pb(\mu-I)_2Pb(PPTA)_2I]$ (2),(3) and [(PPTA)₂Pb(NO₃)₂] (4), of 5-phenyl-3-(pyridin-2-yl)-1,2,4-triazine (PPTA) were prepared and identified by elemental analysis, FT-IR, ¹H NMR spectroscopy and single-crystal X-ray diffraction. All the coordination modes of the 3-(pyridin-2-yl)-1,2,4-triazine-based ligands were studied by CSD software for predicting the behavior of the PPTA ligand in the reaction with metal ions. In the crystal structure of 1, the lead atom has a PbN_4Cl_3 environment with a distorted capped octahedral geometry. Complexes 2 and 3 are also dinuclear and isostructural with 1. The lead atom in the crystal structure of complex 4 has a coordination number of eight and a distorted cube geometry. The metal atom coordination spheres in all four structures tend to be *holodirected* with a decreasing deviation in the series 1-3. The thermodynamic stability of the isolated complexes and their charge distribution patterns were

studied by DFT and NBO analysis. Theoretical studies reveal that the thermodynamic stability for the optimized complex **1** is higher than those of the isostructural complexes **2** and **3**.

Keywords: Lead(II); Triazine; Dinuclear complex; Computational study; Coordination chemistry

1. Introduction

Compounds containing 1,2,4-triazine moieties have been reported to possess a broad spectrum of biological, pharmacological and medicinal properties, such as anti-HIV [1], antitumor [2], enzyme inhibitor [3], DNA binding [4-6], anti-viral inhibitor [7], BSA-binding [5,8], anti-inflammatory [9], analgesic [10], anti-cytokine[11], anti-hypertensive [12], antimalarial [13] and anti-epileptic [14] activities. This class of compounds has been used in metal ion extraction and segregation processes [15,16], in "oxygen atom transfer" reactions [17], as optical chloride sensors [18], as agents for increasing the redox potentials of metal atoms [19], as energetic materials [20], as reagent for the determination of metal ions in natural and waste waters [21], in colorimetric analysis [21], as metal ion transfer agents across a liquid interface [22] and for the construction of MOFs with different degrees of dimensionality [23,24]. Non-linear optical (NLO) properties, CO₂ sorption and magnetic coupling [25] have been reported for some derivatives of these compounds, as well as the enhancement of the luminescence of lanthanides by coordination with these compounds [26] and ligand to metal charge transfers (LMCT) [27]. These moieties can form bi- [28], tri- [29], tetra- [30] or hexanuclear [31] complexes and coordination polymers [32, 33] and play an important role in network stabilization by $\pi \cdots \pi$ interactions [34].

In this work, the preparation, characterization, crystal structure and theoretical studies of the complexes, $[Cl(PPTA)_2Pb(\mu-Cl)_2Pb(PPTA)_2Cl]$ (1), $[Br(PPTA)_2Pb(\mu-Br)_2Pb(PPTA)_2Br]$

(2), $[I(PPTA)_2Pb(\mu-I)_2Pb(PPTA)_2I]$ (3) and $[(PPTA)_2Pb(NO_3)_2]$ (4), with 5-phenyl-3-(pyridin-2-yl)-1,2,4-triazine (PPTA, Scheme 1), are described.

2. Experimental

2.1 Materials and Instrumentation

All starting chemicals and solvents were reagent or analytical grade and used as received. The infrared spectra in the range 4000-400 cm⁻¹ were recorded on KBr pellets with a FT-IR 8400-Shimadzu spectrometer. ¹H NMR spectra were recorded on a Bruker Avance 300 instrument; chemical shifts (δ) are given in parts per million, relative to TMS as an internal standard. The carbon, hydrogen and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The melting points were determined with a Barnsted Electrothermal 9200 electrically heated apparatus.

2.1.1 Synthesis of 5-phenyl-3-(pyridin-2-yl)-1,2,4-triazine (PPTA)

The PPTA ligand was prepared as described in the literature [35] with some modifications. Also, the spectral data of this ligand were not reported and are presented here. 1.36 g (10 mmol) of picolinohydrazonamide dissolved in EtOH (15 mL) was added to a stirred solution of 1.34 g (10 mmol) of 2-oxo-2-phenylacetaldehyde in EtOH (15 mL). The reaction mixture was refluxed for 5 h. All volatile components of the solution were removed by rotary evaporation and the desired ligand extracted with 50 mL boiling water (five times) and filtrated. Yield: 1.52 g, 65%; m. p.: 133 °C. Anal. Calcd for C₁₄H₁₀N₄ (234.26): C, 71.78; H, 4.30; N, 23.92. Found: C, 71.46; H, 4.33; N, 23.66%. IR (KBr, cm⁻¹): 3054 w (ν CH_ar), 1585 w and 1539 s (ν C=N), 1510 s (ν N=N), 1437 m (ν C=C)_{ar}, 753 s and 684 m (γ py). ¹H NMR (300 MHz, DMSO-*d*₆, ppm, Hz) δ : 10.13 (s, 1 H, C²H), 8.85-8.87 (d, 1 H, C¹¹H, J =

3.9), 8.54-8.57 (d, 1 H, C^{14} H, J = 8.1), 8.44-8.47 (d, 2 H, C^{12} H and C^{13} H, J = 6.9), 8.05-8.10 (t, 1 H, C^{8} H, J = 6.9), 7.65-7.67 (d with shoulder, 4 H, C^{6} H, C^{7} H, C^{9} H and C^{10} H, J = 7.2).

2.1.2 Synthesis of $[Cl(PPTA)_2Pb(\mu-Cl)_2Pb(PPTA)_2Cl](1)$

PPTA (0.05 g, 0.2 mmol) and PbCl₂ (0.06 g, 0.2 mmol) were placed in the large arms of a branched tube. Ethanol and water in a ratio of (6:1) 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 while the other was maintained at ambient temperature [36]. After two days, yellow precipitates were formed in the cooler arm and filtered off. The products were moved to the large arms of a branched tube and the arms filled with water. After a week, the yellow crystals that were deposited in the cooler arm were filtered off and dried in air. Yield: 0.034 g, 43%; m. p.: 230 °C. Anal. Calcd for $C_{56}H_{40}Cl_4N_{16}Pb_2$ (1493.22): C, 45.04; H, 2.70; N, 15.01. Found: C, 45.47; H, 2.73; N, 15.35%. IR (KBr, cm⁻¹): 3057 w (ν CH_{ar}), 1595 m and 1545 s (ν C=N), 1511 s (ν N=N), 1484 m (ν C=C)_{ar}, 758 s and 688 m (γ py). ¹H NMR (300 MHz, DMSO-*d*₆, ppm, Hz) δ: 10.14 (s, 1 H, C²H), 8.86 (s with shoulder, 1 H, C¹¹H), 8.55-8.58 (d, 1 H, C¹⁴H, J = 7.8), 8.45-8.47 (d, 2 H, C¹²H and C¹³H, J = 7.2), 8.06-8.11 (t, 1 H, C⁸H, J = 8.1), 7.66-7.68 (d with shoulder, 4 H, C⁶H, C⁷H, C⁹H and C¹⁰H, J = 6.6).

2.1.3 Synthesis of $[Br(PPTA)_2Pb(\mu-Br)_2Pb(PPTA)_2Br]$ (2)

The procedure for the synthesis of **2** was similar to **1**, except that PbCl₂ was replaced by PbBr₂ (0.11 g, 0.3 mmol), 0.3 mmol of PPTA (0. 07 g) and in one step using a branched tube. After two days, the yellow crystals that were deposited in the cooler arm were filtered off and dried in air. Yield: 0.10 g, 84%; m. p.: 256 °C. Anal. Calcd for C₅₆H₄₀Br₄N₁₆Pb₂ (1671.06): C, 40.25; H, 2.41; N, 13.41. Found: C, 40.06; H, 2.37; N, 13.52%. IR (KBr, cm⁻¹): 3056 w (ν CH_{ar}), 1594 m and 1542 s (ν C=N), 1511 s (ν N=N), 1481 m (ν C=C)_{ar}, 758 s and 687 m (γ

py). ¹H NMR (300 MHz, DMSO- d_6 , ppm, Hz) δ : 10.13 (s, 1 H, C²H), 8.87-8.88 (d, 1 H, C¹¹H, J = 4.5), 8.54-8.57 (d, 1 H, C¹⁴H, J = 7.8), 8.43-8.45 (d, 2 H, C¹²H and C¹³H, J = 4.2), 8.05-8.10 (t, 1 H, C⁸H, J = 7.8), 7.66 (s with shoulder, 4 H, C⁶H, C⁷H, C⁹H and C¹⁰H).

2.1.4 Synthesis of $[I(PPTA)_2Pb(\mu-I)_2Pb(PPTA)_2I]$ (3)

The procedure for the synthesis of **3** was similar to **2**, except that PbBr₂ was replaced by PbI₂ (0.3 mmol, 0.14 g). Yellowish crystals were formed after two days in the cooler arm and filtered. Yield: 0.04 g, 29%; m. p.: 256 °C. Anal. Calcd for C₅₆H₄₀I₄N₁₆Pb₂ (1859.07): C, 36.18; H, 2.17; N, 12.06. Found: C, 35.98; H, 2.15; N, 12.12%. IR (KBr, cm⁻¹): 3052 w (ν CH_{ar}), 1590 m and 1542 s (ν C=N), 1511 s (ν N=N), 1475 m (ν C=C)_{ar}, 757 s and 687 m (γ py). ¹H NMR (300 MHz, DMSO-*d*₆, ppm, Hz) δ : 10.14 (s, 1 H, C²H), 8.86-8.88 (d, 1 H, C¹¹H, J = 3.9), 8.55-8.58 (d, 1 H, C¹⁴H, J = 7.3), 8.45-8.48 (d, 2 H, C¹²H and C¹³H, J = 6.3), 8.06-8.11 (t, 1 H, C⁸H, J = 6.0), 7.63-7.70 (m, 4 H, C⁶H, C⁷H, C⁹H and C¹⁰H).

2.1.5 Synthesis of [(PPTA)₂Pb(NO₃)₂] (4)

The procedure for the synthesis of **4** was similar to **2**, except that PbBr₂ was replaced by Pb(NO₃)₂ (0.3 mmol, 0.10 g). After three days, a precipitate was formed in the cooler arm and filtered, then recrystallized from H₂O/EtOH (1:1). Light pink crystals suitable for X-ray diffraction studies were obtained by slow evaporation after three days. Yield: 0.10 g, 80%; m. p.: 260 °C. Anal. Calcd for C₂₈H₂₀N₁₀O₆Pb (799.73): C, 42.05; H, 2.52; N, 17.51. Found: C, 41.96; H, 2.51; N, 17.45%. IR (KBr, cm⁻¹): 3060 w (ν CH_{ar}), 1600 m and 1542 s (ν C=N), 1514 m (ν N=N), 1483 m (ν C=C)_{ar}, 1404 s (ν_4 NO₃), 1261 m (ν_1 NO₃), 1091 m (ν_2 NO₃), 833 m (ν_6 NO₃), 763 s and 691 m (γ py). ¹H NMR (300 MHz, DMSO-*d*₆, ppm, Hz) δ : 10.15 (s, 1 H, C²H), 8.85-8.87 (s with shoulder, 1 H, C¹¹H), 8.56-8.58 (d, 1 H, C¹⁴H, J = 7.8), 8.45-8.48 (d, 2 H, C¹²H and C¹³H, J = 7.8), 8.06-8.11 (t, 1 H, C⁸H, J = 7.8), 7.66-7.68 (m, 4 H, C⁶H, C⁷H, C⁹H and C¹⁰H).

2.2 Crystal structure determination

Suitable crystals of 1-4 were selected in mineral oil and measured on Stoe IPDS-2T (1, 4) or Stoe IPDS (2, 3) diffractometers using graphite-monochromatized Mo- $K\alpha$ radiation, ($\lambda = 0.71073$ Å) at 180 or 213 K, respectively. Numerical absorption corrections were applied to all data sets. The structures were solved by direct methods using SHELXS and refined with SHELXL [37] using last squares minimisation. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in idealized positions. The molecular graphics were drawn with ORTEP-III [38, 39], Mercury [40] and Diamond [41]. Crystallographic data and details of the data collection and structure refinement, selected bond lengths and angles, and hydrogen bond geometries are listed in Tables 1-3, respectively.

2.3 Computational details

All the structures were optimized with the Gaussian 09 software package [42] and calculated for an isolated molecule using Density Functional Theory (DFT) [43] at the B3LYP/LanL2DZ level of theory, including NBO analysis, and B3LYP/6-31+G was used for a scan of the dihedral angle of PPTA. Cif files of complexes **1** and **2** were used as the input files for the theoretical calculations.

3. Results and Discussion

The reaction between PPTA and solutions of lead(II) chloride, lead(II) bromide, lead(II) iodide and lead(II) nitrate in branched tubes provide complexes **1-4**, respectively. The complexes are air-stable and soluble in DMSO.

3.1 Spectroscopic characterization

In the IR spectra of the PPTA ligand and complexes 1-4, the relatively weak absorption bands above 3000 cm⁻¹ are due to the C–H modes of the aromatic rings. Three bands in the range 1500-1600 cm⁻¹ can be assigned to the vibrations of $v(C=N)_{ar}$ and $v(N=N)_{ar}$. In complexes 1-4 these frequencies are shifted by about 1-15 cm⁻¹ to higher frequency compared to those of the free ligand.

Four bands in the IR spectrum of complex **4** near 1404, 1261, 1091 and 833 cm⁻¹ can be assigned to vibrations of the coordinated nitrate groups (vibrations v_4 , v_1 , v_2 and v_6). The difference between the v_4 and the v_1 peak positions is 143 cm⁻¹, which is typical for bidentate nitrate coordination (monodentate nitrate coordination displays a lower splitting) [44,45].

To interpret the NMR spectra of the compounds, all the aromatic carbon atoms of the PPTA ligand are marked in Scheme 1. The NMR spectra of all the compounds were recorded in DMSO- d_6 and are consistent with the presence of the PPTA ligand. The ¹H NMR spectrum of the ligand shows peaks in the range δ 7.65-10.13 ppm, confirming the aromatic property of PPTA. A singlet peak at the lowest magnetic field was assigned to the only hydrogen atom of the triazine ring. With increasing magnetic field, a doublet peak belonging to the hydrogen atom of C¹¹, the nearest atom to the nitrogen atom of the pyridine ring, is revealed. The peaks belonging to the other hydrogen atoms of the pyridine ring appear in the range δ 8.47-8.57 ppm. The hydrogen atoms of the phenyl ring are observed at a higher magnetic field (δ 7.65–8.10 ppm) than the triazine and pyridine ring hydrogen atoms. Comparing the ¹H NMR spectra of complexes **1-4** with that of the ligand does not show any significant shift due to complexation. A similar result was also observed in the IR spectroscopy studies.

3.2 Description of the crystal structures

3.2.1 Crystal structures of $[Cl(PPTA)_2Pb(\mu-Cl)_2Pb(PPTA)_2Cl]$ (1), $[Br(PPTA)_2Pb(\mu-Br)_2Pb(PPTA)_2Br]$ (2) and $[I(PPTA)_2Pb(\mu-I)_2Pb(PPTA)_2I]$ (3)

X-ray structure analysis of complexes of **1-3** revealed that these complexes are isostructural molecules, thus a discussion about their structures is combined. In the crystal structures of complexes **1-3** (Figure 1, for complex **1**), the lead atom is coordinated by four nitrogen atoms of two ligands and by three halide ions (chloride, bromide and iodide for **1-3**, respectively), with a coordination number seven and a distorted capped octahedral geometry (Figure 2, for complex **1**). Searching the Cambridge Structural Database (CSD) [46] revealed that there is no example for lead atoms with PbN₄Cl₃ (complex **1**) and PbN₄Br₃ (complex **2**) environments. The average of both Pb–N_{py} bond lengths (2.785 Å for **1**, 2.772 Å for **2**) is slightly shorter than the average of the two Pb–N_{triazine} bond lengths (2.817 Å for **1**, 2.784 Å for **2**). A structural study of the literature data revealed that there is only one example for the PbN₄I₃ environment, which has a polymeric structure with two bridging iodide ions between the lead atoms [47]. The average Pb–N_{py} and Pb–I_{bridging} distances in **3** (2.755 and 3.354 Å, respectively) are larger than in the reported structure (2.617 and 3.244 Å), while the Pb–I_{terminal} bond length (3.050 Å) is similar to this analogue (3.091 Å).

In iodide complex **3**, both Pb–N_{py} as well as both Pb–N_{triazine} bond lengths are similar (the differences of the Pb–N_{py} and Pb–N_{triazine} bond lengths are 0.03 and 0.07 Å, respectively). In contrast, in the chloride complex **1** there are significant differences. Both Pb–N_{py} and both Pb–N_{triazine} distances differ by 0.22 and 0.19 Å, respectively. In complex **2** the situation is intermediate (0.16 and 0.11 Å, respectively, for the Pb–N_{py} and Pb–N_{triazine} distance difference). This observation is typical for complexes of central atoms with lone pairs. For heavier atoms (central atoms and donor atoms) the distortion is less pronounced than for lighter atoms. The distortion is stronger in the chloride complex, only small or not present in the iodide complex, and can be attributed to varying degrees of stereochemical activity of the Pb²⁺ lone pair. Based on these observations, we can conclude that the *holodirected* character is increasing on going from complex **1** to complex **3**.

There are two types of halide ligands in the crystal structures of **1-3**, asymmetrically bridging and terminally bound. A mean plane through all four halide ligands and two lead atoms revealed that these atoms are not exactly co-planar (the r.m.s. deviation is 0.247, 0.204 and 0.076 Å for Pb1, respectively for **1-3**) but with the increasing ionic radius of the halide ligands the lead atoms tend to lie in a plane with the halide ions. The bond lengths of the asymmetrically bridging halides are significantly longer than for the terminal ones. Again, the difference in bond lengths Pb1-X1 *vs*. Pb1-X1^{*i*} (X = Cl, Br, I) decreases from complex **1** (0.388 Å) to **3** (0.196 Å). Complexes **1-3** are centrosymmetric with a center of inversion at the center of the Pb1/X1/Pb1^{*i*}/X1^{*i*} plane.

PPTA acts as bidentate ligand, forming five-membered chelate rings with the lead atoms. The average of the dihedral angles between the pyridine and triazine rings in both coordinated ligands in **1** is 8.17°, confirming that these rings are approximately coplanar. For all coordinated 3-(pyridin-2-yl)-1,2,4-triazine-based ligands this value was determined to be in the range 0.58–21.22°. 3-(Pyridin-2-yl)-1,2,4-triazine-based ligands can coordinate to metal atoms in three ways, which are presented in Scheme 2. A study of this type of ligand revealed that the coordination mode A (116 hits), which was observed in complexes **1-3**, is more common than the modes B (14 hits) and C (3 hits). A structural investigation of ligands of mode B showed that most of them have another pyridine ring or O-donor groups on the C1 atom of the triazine ring (Scheme 1) [26,28,48-51], thus they can form two chelate rings and be more stable than in mode A. All three examples of coordination mode C are di- or polynuclear [28,52,53].

3.2.2 Crystal structure of $[(PPTA)_2Pb(NO_3)_2](4)$

X-ray structure analysis of complex **4** (Figure 3) revealed that the geometry around the lead atom is distorted cubic (Figure 4), by coordination of four nitrogen atoms belonging to

two PPTA ligands and four oxygen atoms of two nitrate ions. There are four examples for a PbN_4O_4 environment in the CSD, in which the oxygen atoms belong to bidentate nitrate ligands and all the nitrogen atoms are in aromatic rings. The average of bond lengths and angles for these four complexes are presented in Scheme 3. The Pb–N_{py} and Pb–O bond lengths of **4**, on average 2.668 and 2.768 Å respectively, are larger and shorter than those of the CSD average, respectively. Comparing the bond angles of the chelate rings formed by the nitrate ions with the CSD average revealed that the angles in **4** (45.97°) are about 1° larger. In complex **4** the distortion from the complex being *holodirected* is evident (differences of 0.14 and 0.16 Å, respectively, for the Pb–N_{py} and Pb–N_{triazine} distances). A search through all the lead complexes containing coordinated nitrate ions by CSD software was done, revealing that the coordination mode of the nitrate ligands in **4** is common for lead(II) atoms (Figure 5).

3.2.3 Crystal network interactions

In the crystal network of **1**, **2** and **3** (Figure 6, for complex **3**) intermolecular C–H…N and C–H…X (X = Cl, Br, I) hydrogen bonds appear between adjacent complexes. Among the two uncoordinated nitrogen atoms of the triazine ring, the N1 atom (Scheme 1) participates in hydrogen bonding while the other, N3, does not have any interactions. In this way, the nitrogen and halide ions act as proton acceptors whereas the carbon atoms participate in hydrogen bonding as proton donors. In addition to hydrogen bonds, the crystal networks of **1**-**3** are further stabilized by π – π stacking interactions between the aromatic rings of adjacent ligands. In this pattern, the rings are not exactly on top of each other, the pyridine and triazine rings of one ligand are close to the benzene and triazine rings on the adjacent ligand, respectively. There are additional π – π interactions between the triazole ring (N2, N3, N4, C6, C7, C8) and a phenyl group (C9–C14) of a symmetry equivalent ligand. In the crystal network of complex **4** (Figure 7), the nitrogen atoms of the PPTA ligands do not participate

in hydrogen bonding, while the oxygen atoms of the nitrate ions play an important role in crystal network interactions. In this network, there are π - π interactions between two symmetry equivalent ligands with some offset, e.g., C6…C13', 3.361(9), N4…C14' and N4'…C14, 3.311(8) Å.

3.3 Theoretical studies on PPTA and its complexes 1-3

An investigation of the CSD database revealed that the dihedral angle between the triazine and pyridine rings is variable. For a theoretical study of this dihedral angle, the geometrical coordinates of PPTA were optimized using the DFT method, then the energy level of the free ligand for different dihedral angles was calculated in about 1800 scans (Figure 8). The DFT calculations revealed that when the dihedral angle between the pyridine and triazine rings is zero and the nitrogen atom of the pyridine ring (N4) is near to the N3 atom of the triazine ring (Scheme 1), the PPTA is in the most stable conformation. With increasing dihedral angles, the energy level of the ligand is increased and maximum energy corresponds to a dihedral angle of 91.7°. The energy barrier for rotation of the pyridine ring about the C_{py} - $C_{triazine}$ bond and converting the two isomers is 5.2 kcal/mol (for isolated molecules, not for the solid state). Studying the CSD entries revealed that both isomers have been observed for uncoordinated 3-(pyridin-2-yl)-1,2,4-triazine-based ligands [54-58].

For comparing the energy level of the different halido dinuclear complexes, for one isolated molecule, DFT calculations were performed. These data reveal that the thermodynamic stability of the lead complex containing chloride ions and PPTA ligands (-1945526 kcal/mol) is higher than that of the isostructural complexes containing bromide or iodide ions (-1941050 and -1936574 kcal/mol for 2^{opt} and 3^{opt} , respectively).

Similarly to the X-ray structure analysis results, in the optimized structures the differences between both Pb– N_{py} (0.06 Å) and both Pb– $N_{triazine}$ bond lengths (0.05 Å) in the

iodide complex (3^{opt}) is not considerable, while for the two others it is significant (0.19 and 0.08 Å for 1^{opt} , 0.18 and 0.12 Å for 2^{opt}) confirming the distorted *holodirected* environment for complexes of 1^{opt} and 2^{opt} in their isolated form.

For studying the charge distribution before and after complexation, an NBO analysis was done on the free PPTA molecule and its complexes (Table 4). The results reveal that the calculated charge on the lead atom is about +1, lower than the formal charge (+2). Based on the calculated charge average for the same atoms (Table 4) of the ligand and the complexes, the charges on the coordinated atoms, N2 and N3 and also the non-coordinated N4 atom (Scheme 1) become negative after coordination. The charges of the N1 (Scheme 1), hydrogen and carbon atoms in the complexes are more positive than in the free ligand. In the complexes, the LUMO is delocalized on the ligand, except the pyridine ring, while the HOMO is delocalized on the metal center and halide ions, without any significant participation of the ligand molecule (Table 5).

4. Conclusions

Complexes 5-phenyl-3-(pyridin-2-yl)-1,2,4-triazine (PPTA), namely $[Cl(PPTA)_2Pb(\mu-Cl)_2Pb(PPTA)_2Cl]$ $[Br(PPTA)_2Pb(\mu-Br)_2Pb(PPTA)_2Br]$ (1), (2), $[I(PPTA)_2Pb(\mu-I)_2Pb(PPTA)_2I]$ (3) and $[(PPTA)_2Pb(NO_3)_2]$ (4), were synthesized and their spectral (IR, ¹H NMR) and structural properties were investigated. In the crystal structure of 1, with C_i symmetry, the lead atom is coordinated by four nitrogen atoms of two PPTA ligands and three chloride ions in a distorted capped octahedral environment. Complexes 2 and **3** are isostructural to **1**, with PbN₄Br₃ and PbN₄I₃ environments, respectively. Based on the differences between similar bond lengths around the lead atom, the coordination sphere of 1 and 2 is distorted *holodirected*, with increasing *holodirected* character from 1 to 3. The coordination number of the lead(II) atom in the crystal structure of 4 is eight, which is filled

by four nitrogen atoms of two PPTA ligands and four oxygen atoms of two chelating nitrate ions. The geometry around the lead atom in **4** is distorted cube-like and the arrangement of the donor atoms is distorted *holodirected*. A structural study of 3-(pyridin-2-yl)-1,2,4triazine-based ligands revealed that these units have been observed in three coordination modes and among them the formation of chelate rings by the N4_{py} and N2_{triazine} atoms is the most common. A theoretical study revealed that the chloride binuclear complexes of PbX₂ (X = Cl, Br, I) with PPTA are thermodynamically more stable than the other complexes. NBO analysis shows that the charge on the N1, hydrogen and carbon atoms of PPTA and also the halide ions becomes positive after coordination.

Appendix A. Supplementary data

CCDC 1534865, 1521988, 1521987 and 1521986 respectively for 1-4 complexes contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] V. Béreau, J. Rey, E. Deydier, J. Marrot, Inorg. Chem. Acta, 351 (2003) 389-394.

[2] L. Yurttaş, Ş. Demirayak, S. Ilgın, Ö. Atlı, Bioorg. Med. Chem., 22 (2014) 6313-6323.

[3] J. Chen, X. Wang, Y. Shao, J. Zhu, Y. Zhu, Y. Li, Q. Xu, Z. Guo, Inorg. Chem., 46 (2007) 3306-3312.

[4] K. Abdi, H. Hadadzadeh, M. Salimi, J. Simpson, A.D. Khalaji, Polyhedron, 44 (2012) 101-112.

[5] M. Anjomshoa, H. Hadadzadeh, M. Torkzadeh-Mahani, S.J. Fatemi, M. Adeli-Sardou, H.A. Rudbari, V.M. Nardo, Eur. J. Med. Chem., 96 (2015) 66-82.

[6] X.L. Wang, H. Chao, H. Li, X.L. Hong, L.N. Ji, X.Y. Li, J. Inorg. Biochem., 98 (2004) 423-429.

[7] J.G. Małecki, B. Machura, A. Świtlicka, Struct. Chem., 22 (2011) 77-87.

[8] M. Anjomshoa, H. Hadadzadeh, S.J. Fatemi, M. Torkzadeh-Mahani, Spectrochim. Acta, A136 Pt B (2015) 205-215.

[9] H. Irannejad, A. Kebriaieezadeh, A. Zarghi, F. Montazer-Sadegh, A. Shafiee, A. Assadieskandar, M. Amini, Bioorg. Med. Chem., 22 (2014) 865-873.

[10] H.M. Ashour, O.G. Shaaban, O.H. Rizk, I.M. El-Ashmawy, Eur. J. Inorg. Chem., 62 (2013) 341-351.

[11] M. Khoshneviszadeh, M.H. Ghahremani, A. Foroumadi, R. Miri, O. Firuzi, A. Madadkar-Sobhani, N. Edraki, M. Parsa, A. Shafiee, Bioorg. Med. Chem., 21 (2013) 6708-6717.

[12] W.P. Heilman, R.D. Heilman, J.A. Scozzie, R.J. Wayner, J.M. Gullo, Z.S. Ariyan, J. Med. Chem., 22 (1979) 671-677.

[13] A. Agarwal, K. Srivastava, S.K. Puri, P.M.S. Chauhan, Bioorg. Med. Chem. Lett., 15 (2005) 531-533.

[14] P. Ahuja, N. Siddiqui, Eur. J. Inorg. Chem., 80 (2014) 509-522.

[15] G.L. Guillet, I.F.D. Hyatt, P.C. Hillesheim, K.A. Abboud, M.J. Scott, New J. Chem., 37 (2013) 119-131.

[16] P.B. Iveson, C. Riviere, D. Guillaneux, M. Nierlich, P. Thuery, M. Ephritikhine, C. Madic, Chem. Commun., (2001) 1512-1513.

[17] S. Das, A. Chakravorty, Eur. J. Inorg. Chem., 2006 (2006) 2285-2291.

[18] T. Riis-Johannessen, K. Schenk, K. Severin, Inorg. Chem., 49 (2010) 9546-9553.

[19] R. Uma, M. Palaniandavar, R.J. Butcher, Dalton Trans., (1996) 2061-2066.

[20] D. Frem, Combust. Explo. Shock, 50 (2014) 441-446.

[21] P.L. Croot, K.A. Hunter, Anal. Chim. Acta, 406 (2000) 289-302.

[22] H. Katano, H. Kuboyama, M. Senda, J. Electroanal. Chem., 483 (2000) 117-123.

[23] A.M. Fedosseev, M.S. Grigoriev, I.A. Charushnikova, N.A. Budantseva, Z.A. Starikova, P. Moisy, Polyhedron, 27 (2008) 2007-2014.

[24] B. Machura, R. Kruszynski, J. Kusz, J. Kłak, J. Mroziński, Polyhedron, 26 (2007) 4427-4435.

[25] A.O. Ibrahim, Y. Zhou, F. Jiang, L. Chen, X. Li, W. Xu, O.O.E. Onawumi, O.A. Odunola, M. Hong, Eur. J. Inorg. Chem., 2011 (2011) 5000-5005.

[26] L. Panayiotidou, M. Stylianou, N. Arabatzis, C. Drouza, P. Lianos, E. Stathatos, A.D. Keramidas, Polyhedron, 52 (2013) 856-865.

[27] B. Machura, A. Świtlicka, R. Kruszynski, J. Mroziński, J. Kłak, J. Kusz, Polyhedron, 27 (2008) 2959-2967.

[28] F. Marandi, N. Hosseini, H. Krautscheid, D. Lässig, J. Lincke, M. Rafiee, Y.A. Asl, J. Mol. Struct., 1006 (2011) 324-329.

[29] L. Li, M.M. Turnbull, J. Ackers, J. Chen, H. Lin, B. Pan, H. Wang, B.M. Foxman, Inorg. Chem. Acta, 362 (2009) 3845-3852.

[30] X.-H. Zou, J.-W. Cai, X.-L. Feng, X.-P. Hu, G. Yang, H. Zhang, L.-N. Ji, Transition Met. Chem., 26 (2001) 704-708.

[31] E. López-Torres, M.A. Mendiola, C.J. Pastor, Inorg. Chem., 45 (2006) 3103-3112.

[32] Q. Ma, M. Zhu, L. Lu, S. Feng, T. Wang, Dalton Trans., 39 (2010) 5877-5884.

[33] Y.-F. Wang, L. Zhuo, Y.-C. Sun, J.-S. Zhao, L.-Y. Wang, CrystEngComm, 15 (2013) 9980-9987.

[34] N.E. Eltayeb, T.S. Guan, B.M. Yamin, Acta Crystallogr., E62 (2006) m2284-m2286.

[35] V. Maheshwari, D. Bhattacharyya, F.R. Fronczek, P.A. Marzilli, L.G. Marzilli, Inorg Chem, 45 (2006) 7182-7190.

[36] F. Marandi, F. Amoopour, I. Pantenburg, G. Meyer, J. Mol. Struct., 973 (2010) 124-129.

[37] G. Sheldrick, Acta Crystallogr., A64 (2008) 112-122.

[38] L.J. Farrugia, J. Appl. Crystallogr., 30 (1997) 565-565.

[39] M.N. Burnett, C.K. Johnson, ORTEP-III, Report ORNL-6895. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S., 1996.

[40] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. Van De Streek, P.A. Wood, J. Appl. Crystallogr., 41 (2008) 466-470.

[41] G. Bergerhof, M. Berndt, K. Brandenburg, J. Res. Natl. Stand. Technol., 101 (1996) 221–225.

[42] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G.

Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, in, Gaussian, Inc., Wallingford, CT, USA, 2009.

[43] J.P. Perdew, Phys. Rev., B33 (1986) 8822-8824.

[44] M. Hakimi, K. Moeini, Z. Mardani, M.A. Fernandes, F. Mohr, E. Schuh, J. Coord. Chem., 65 (2012) 1232-1245.

[45] M. Hakimi, K. Moeini, Z. Mardani, E. Schuh, F. Mohr, J. Coord. Chem., 66 (2013) 1129-1141.

[46] F.H. Allen, Acta Crystallogr., B58 (2002) 380-388.

[47] L. Saghatforoush, A. Bakhtiari, H. Gheleji, J. Solid State Chem., 221 (2015) 433-440.

[48] F. Marandi, H.-K. Fun, J. Coord. Chem., 62 (2009) 1972-1979.

[49] A.M. Prokhorov, D.N. Kozhevnikov, V.L. Rusinov, O.N. Chupakhin, G.G. Aleksandrov, Y.N. Shvachko, D.V. Starichenko, A.V. Korolev, D.V. Bukhvalov, V.V. Ustinov, Russ. Chem. Bull., 57 (2009) 561-566.

[50] A.M. Prokhorov, P.A. Slepukhin, D.N. Kozhevnikov, J. Organomet. Chem., 693 (2008) 1886-1894.

[51] A. Bhattacharyya, P.M. Forster, D.B. Rego, K.R. Czerwinski, Eur. J. Inorg. Chem., 2016 (2016) 921-927.

[52] F.-R. Dai, Y.-H. Wu, L.-Y. Zhang, B. Li, L.-X. Shi, Z.-N. Chen, Eur. J. Inorg. Chem., 2011 (2011) 2306-2316.

[53] D.N. Kozhevnikov, V.N. Kozhevnikov, A.M. Prokhorov, M.M. Ustinova, V.L. Rusinov, O.N. Chupakhin, G.G. Aleksandrov, B. König, Tetrahedron Lett., 47 (2006) 869-872.

[54] N.E. Eltayeb, S.G. Teoh, S.-L. Ng, H.-K. Fun, K. Ibrahim, Acta Crystallogr., E63 (2007) o1041-o1042.

[55] N.E. Eltayeb, S.G. Teoh, S. Chantrapromma, H.-K. Fun, K. Ibrahim, Acta Crystallogr., E63 (2007) 03792-03793.

[56] K. Lyczko, S. Ostrowski, Nukleonika, 60 (2015) 853-857.

[57] F.W. Lewis, L.M. Harwood, M.J. Hudson, M.G. Drew, J.F. Desreux, G. Vidick, N. Bouslimani, G. Modolo, A. Wilden, M. Sypula, T.H. Vu, J.P. Simonin, J. Am. Chem. Soc., 133 (2011) 13093-13102.

[58] M.R. Foreman, M.J. Hudson, M.G. Drew, C. Hill, C. Madic, Dalton Trans., (2006) 1645-1653.

	1	2	3	4
Empirical formula	$C_{56}H_{40}Cl_4N_{16}Pb_2$	$C_{56}H_{40}Br_4N_{16}Pb_2$	$C_{56}H_{40}I_4N_{16}Pb_2$	$C_{28}H_{20}N_{10}O_6Pb$
Formula weight, g	1493.22	1671.06	1859.07	799.73
mol ⁻¹				
Crystal size. mm ³	0.17 imes 0.10 imes 0.07	0.30 imes 0.22 imes 0.07	0.15 imes 0.04 imes 0.04	$0.35 \times 0.05 \times 0.000$
Temperature, K	180	213	213	180
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$\frac{12}{a}$	12/a	12/a	$\overline{P}1$
Unit cell dimensions	12,0	12/0	120	
a Å	14 1202(6)	14 2287(5)	14 1275(7)	8 8484(9)
h Å	14 3363(5)	14 7617(6)	15 0880(8)	9 7060(9)
c Å	26 2550(13)	26 3850(8)	27 3051(11)	16 6948(16)
a °	90.00	90.00	90.00	76 683(7)
ρ. ο	07 258(2)	90.00	90.00	70.083(7)
ρ, °	97.538(5)	98.230(4)	99.715(5)	80.921(8) 85.100(8)
γ, ·	90.00	90.00	90.00	85.109(8)
volume, A	52/1.1(4)	5484.7(3)	5/30.8(5)	13/6.0(2)
	4	4	4	2
Calculated density, -3	1.882	2.024	2.152	1.930
g cm				
Absorption	6.64	9.10	8.07	6.20
coefficient, mm ⁻¹				
<i>F</i> (000), e	2880	3168	3456	776
θ range for data	2.0-28.0	2.4-27.6	2.6-28.0	2.1–27.9
collection, deg				
h, k, l ranges	$-18 \le h \le 17, -18 \le k$	$-18 \le h \le 18, -19 \le k$	$-18 \le h \le 18, -19 \le k$	$-10 \le h \le 11, -12$
	$\leq 18, -34 \leq l \leq 34$	$\leq 19, -34 \leq l \leq 34$	$\leq 19, -35 \leq 1 \leq 31$	$\leq 12, -21 \leq l \leq 2$
Reflections	35561 / 6060 / 0.045	21242 / 6073 / 0.043	22831 / 6743 / 0.050	11669 / 5916 / 0.
collected /				
independent / R _{int}				
Data / restraints /	6060 / 0 / 352	6073 / 0 / 352	6743 / 0 / 352	5916 / 0 / 407
parameters				
Goodness-of-fit on	0.83	0.76	0.69	0.90
F^2				
$R1 / wR2 (I > 2 \sigma(I))$	0.0175 / 0.0301	0.0217/0.0335	0.0278 / 0.0481	0.0322/0.0589
R1 / wR2 (all data)	0.0301/0.0313	0.0422 / 0.0354	0.0589 / 0.0511	0.0516/0.0625
Largest diff_neak /	0.050170.0515	0.64 / -0.54	1.00 / -0.48	1.03 / -1.47
hole e $Å^{-3}$	0.707 1.04	0.047 0.04	1.007 0.40	1.05/ 1.4/
Largest diff. peak / hole, e $Å^{-3}$	0.70/-1.04	0.64 / -0.54	1.00 / -0.48	1.03 / -1.47

Table 1. Crystal and structure refinement data for complexes 1-4.

Pb1-Cl1 2.8276(6) Pb1-Br1 3.0026(4) Pb1-II 3.2556(8) Pb1-N1 2.599(3) Pb1-Cl1' 3.2157(7) Pb1-Br1' 3.3057(4) Pb1-II' 3.4516(6) Pb1-N2 2.545(4) Pb1-Cl2 2.6636(9) Pb1-Br2 2.8157(6) Pb1-I2 3.0504(6) Pb1-N5 2.736(4) Pb1-N1 2.674(2) Pb1-N1 2.692(3) Pb1-N1 2.770(5) Pb1-N6 2.731(4) Pb1-N2 2.722(2) Pb1-N5 2.851(3) Pb1-N5 2.740(5) Pb1-O1 2.873(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N5 2.740(5) Pb1-O3 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) Cl1-Pb1-Cl2 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-N1 85.7(1) N1-Pb1-N2 63.2(1) Cl1-Pb1-N1 86.79(5) Br1-Pb1-N5 85.7(1) N1-Pb1-N5 165.7(1) Cl1-Pb1-N5 84.69(5) Br1-Pb	Pbil-Cl1 2.8276(6) Pbil-Brl 3.0026(4) Pbil-II 3.2556(8) Pbil-N1 2.599(3) Pbil-Cl1 ⁱ 3.2157(7) Pbil-Brl ⁱ 3.3057(4) Pbil-II ⁱ 3.4516(6) Pbil-N2 2.545(4) Pbil-Cl2 2.6636(9) Pbil-Brl ² 2.8157(6) Pbil-12 3.0504(6) Pbil-N5 2.736(4) Pbil-N1 2.674(2) Pbil-N1 2.692(3) Pbil-N1 2.770(5) Pbil-N6 2.708(5) Pbil-N2 2.722(2) Pbil-N2 2.731(3) Pbil-N2 2.781(5) Pbil-O1 2.873(4) Pbil-N5 2.895(2) Pbil-N5 2.851(3) Pbil-N5 2.740(5) Pbil-O3 2.697(4) Pbil-N6 2.912(2) Pbil-N6 2.836(3) Pbil-N6 2.711(4) Pbil-O5 2.809(4) Cl1-Pbil-Cl2 92.44(2) Brl-Pbil-N1 86.74(7) II-Pbil-N1 85.7(1) NI-Pbil-N2 63.2(1) Cl1-Pbil-N2 143.47(5) Brl-Pbil-N5 83.03(9) NI-Pbil-N6 180.2(1) Cl1-Pbil-N5 <th></th> <th>1</th> <th></th> <th>2</th> <th></th> <th>3</th> <th></th> <th>4</th> <th></th>		1		2		3		4	
Pbi-Cl1 ⁱ 3.2157(7) Pbi-Br1 ⁱ 3.3057(4) Pbi-I ¹ 3.4516(6) Pbi-N2 2.545(4) Pbi-Cl2 2.6636(9) Pbi-Br2 2.8157(6) Pbi-L2 3.0504(6) Pbi-N5 2.736(4) Pbi-N1 2.674(2) Pbi-N1 2.692(3) Pbi-N1 2.770(5) Pbi-N6 2.736(4) Pbi-N2 2.722(2) Pbi-N5 2.851(3) Pbi-N5 2.740(5) Pbi-O1 2.873(4) Pbi-N5 2.895(2) Pbi-N5 2.851(3) Pbi-N5 2.697(4) Pbi-N6 2.912(2) Pbi-N6 2.836(3) Pbi-N6 2.711(4) Pbi-O5 2.809(4) Pbi-N6 2.912(2) Pbi-N6 2.836(3) Pbi-N6 2.710(5) Pbi-O6 2.697(4) C11-Pbi-N1 86.79(5) Br1-Pbi-Br1 8.67(7) I1-Pbi-N1 8.67(7) N1-Pbi-N1 8.67(7) <t< td=""><td>Section Pb1-Cl1ⁱ 3.2157(7) Pb1-Br1ⁱ 3.3057(4) Pb1-lⁱ 3.4516(6) Pb1-N2 2.545(4) Pb1-Cl2 2.6636(9) Pb1-Br2 2.8157(6) Pb1-12 3.0504(6) Pb1-N5 2.736(4) Pb1-N1 2.674(2) Pb1-N1 2.692(3) Pb1-N1 2.770(5) Pb1-N6 2.738(4) Pb1-N2 2.722(2) Pb1-N2 2.731(3) Pb1-N5 2.740(5) Pb1-01 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.851(3) Pb1-N5 2.740(5) Pb1-03 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N5 2.740(5) Pb1-03 2.697(4) C11-Pb1-Cl2 92.44(2) Br1-Pb1-Br2 92.87(2) I1-Pb1-N1 8.7(1) N1-Pb1-N2 163.01(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N1 83.81(1) N1-Pb1-N6 163.01(1)<</td><td></td><td>Pb1-Cl1</td><td>2.8276(6)</td><td>Pb1–Br1</td><td>3.0026(4)</td><td>Pb1-I1</td><td>3.2556(8)</td><td>Pb1-N1</td><td>2.599(3)</td></t<>	Section Pb1-Cl1 ⁱ 3.2157(7) Pb1-Br1 ⁱ 3.3057(4) Pb1-l ⁱ 3.4516(6) Pb1-N2 2.545(4) Pb1-Cl2 2.6636(9) Pb1-Br2 2.8157(6) Pb1-12 3.0504(6) Pb1-N5 2.736(4) Pb1-N1 2.674(2) Pb1-N1 2.692(3) Pb1-N1 2.770(5) Pb1-N6 2.738(4) Pb1-N2 2.722(2) Pb1-N2 2.731(3) Pb1-N5 2.740(5) Pb1-01 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.851(3) Pb1-N5 2.740(5) Pb1-03 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N5 2.740(5) Pb1-03 2.697(4) C11-Pb1-Cl2 92.44(2) Br1-Pb1-Br2 92.87(2) I1-Pb1-N1 8.7(1) N1-Pb1-N2 163.01(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N1 83.81(1) N1-Pb1-N6 163.01(1)<		Pb1-Cl1	2.8276(6)	Pb1–Br1	3.0026(4)	Pb1-I1	3.2556(8)	Pb1-N1	2.599(3)
opped Pb1-Cl2 2.6636(9) Pb1-Br2 2.8157(6) Pb1-12 3.0504(6) Pb1-N5 2.736(4) Pb1-N1 2.674(2) Pb1-N1 2.692(3) Pb1-N1 2.770(5) Pb1-N6 2.708(5) Pb1-N2 2.722(2) Pb1-N5 2.851(3) Pb1-N2 2.781(5) Pb1-O1 2.873(4) Pb1-N5 2.895(2) Pb1-N5 2.851(3) Pb1-N5 2.740(5) Pb1-O3 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.835(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N5 2.697(4) C11-Pb1-N1 86.70(5) Br1-Pb1-Br2 92.77(2) I1-Pb1-N2 93.66(2) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 85.6(1) C11-Pb1-N3 84.69(5) Br1-Pb1-N5 83.7(6) I1-Pb1-N5 85.3(3) N1-Pb1-N5 85.3(1) N1-Pb1-N5 85.3(1) N1-Pb1-N5	Section Pb1-Cl2 2.6363(9) Pb1-Br2 2.8157(6) Pb1-12 3.0504(6) Pb1-N5 2.736(4) Pb1-N1 2.674(2) Pb1-N1 2.692(3) Pb1-N1 2.770(5) Pb1-N6 2.708(5) Pb1-N2 2.722(2) Pb1-N2 2.731(3) Pb1-N2 2.781(5) Pb1-O1 2.873(4) Pb1-N5 2.895(2) Pb1-N5 2.851(3) Pb1-N6 2.740(5) Pb1-O3 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-N1 8.67(1) N1-Pb1-N2 2.697(6) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 160.6(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O5 79.2(1		Pb1–Cl1 ⁱ	3.2157(7)	Pb1–Br1 ^{<i>i</i>}	3.3057(4)	Pb1–I1 ^{<i>i</i>}	3.4516(6)	Pb1-N2	2.545(4)
PBI-N1 2.674(2) Pb1-N1 2.692(3) Pb1-N1 2.770(5) Pb1-N6 2.708(5) Pb1-N2 2.722(2) Pb1-N2 2.731(3) Pb1-N2 2.781(5) Pb1-O1 2.873(4) Pb1-N5 2.895(2) Pb1-N5 2.851(3) Pb1-N5 2.740(5) Pb1-O3 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-N1 85.7(1) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 63.2(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 136.(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N5 85.03(9) N1-Pb1-O3 76.7(1)	Segure Pb1-N1 2.674(2) Pb1-N1 2.692(3) Pb1-N1 2.770(5) Pb1-N6 2.708(5) Pb1-N2 2.722(2) Pb1-N2 2.731(3) Pb1-N2 2.781(5) Pb1-O1 2.873(4) Pb1-N5 2.895(2) Pb1-N5 2.851(3) Pb1-N5 2.740(5) Pb1-O3 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-N1 85.7(1) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-Br1 81.09(1) I1-Pb1-N5 83.3(1) N1-Pb1-O5 7		Pb1-Cl2	2.6636(9)	Pb1-Br2	2.8157(6)	Pb1-I2	3.0504(6)	Pb1-N5	2.736(4)
Pb1-N2 2.722(2) Pb1-N2 2.731(3) Pb1-N2 2.781(5) Pb1-O1 2.873(4) Pb1-N5 2.895(2) Pb1-N5 2.851(3) Pb1-N5 2.740(5) Pb1-O3 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) Pb1-N1 86.79(5) Br1-Pb1-Br2 92.77(2) I1-Pb1-N1 85.7(1) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N1 85.03(9) N1-Pb1-N6 105.6(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N5 85.03(9) N1-Pb1-O5 79.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-Br1 ¹ 81.09(1) I1-Pb1-N6 138.3(1) N1-Pb1-O5 79.2(1) C11-Pb1-C11 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-N6 138.3(1) N1-Pb1-O5 79.2(Pb1-N2 2.722(2) Pb1-N2 2.731(3) Pb1-N2 2.781(5) Pb1-O1 2.873(4) Pb1-N5 2.895(2) Pb1-N5 2.851(3) Pb1-N5 2.740(5) Pb1-O3 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-I2 93.66(2) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N5 85.03(9) N1-Pb1-O3 76.7(1) C11-Pb1-N6 134.17(5) Br1-Pb1-Br1 ² 98.91(2) Pb1-11-Pb1 81.12(1) N1-Pb1-O5 79.2	lces	Pb1–N1	2.674(2)	Pb1-N1	2.692(3)	Pb1-N1	2.770(5)	Pb1-N6	2.708(5)
Link Pb1-N5 2.895(2) Pb1-N5 2.851(3) Pb1-N5 2.740(5) Pb1-O3 2.697(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.609(4) Pb1-N1 Score Score Score Score Score Pb1-O6 2.691(6) C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-N1 85.7(1) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N6 138.3(1) N1-Pb1-O5 79.2(1) C11-Pb1-C11 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-N6 138.3(1) N1-Pb1-O6 104.1(1	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	istar	Pb1-N2	2.722(2)	Pb1-N2	2.731(3)	Pb1-N2	2.781(5)	Pb1-O1	2.873(4)
Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-I2 93.66(2) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) Pb1-C11-Pb1 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-N1 81.12(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1)	Pb1-N6 2.912(2) Pb1-N6 2.836(3) Pb1-N6 2.711(4) Pb1-O5 2.809(4) C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-I2 93.66(2) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.7(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) C11-Pb1-C1i ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-N ⁱ 81.12(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O5 79.2(1) i : 0.5 - x, 1.5 - y, 1.5 - z i : 0.5 - x, 1.5 - y, 1.5 - z i : 0.5 - x, 1.5 - y, 1.5 - z i : 0.5 -	Д	Pb1-N5	2.895(2)	Pb1-N5	2.851(3)	Pb1-N5	2.740(5)	Pb1-O3	2.697(4)
Seperation C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-I2 93.66(2) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) C11-Pb1-C11 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-N6 138.3(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 89.91(2) Pb1-11-Pb ⁱ 88.8(1) N1-Pb1-O6 104.1(1) O1-Pb1-O5 77.3(1) 10-Pb1-O5 77.3(1) 10-Pb1-O5 77.3(1) i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y,	Vertice C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-I2 93.66(2) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) C11-Pb1-C11 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-N6 138.3(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 89.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O5 79.2(1) Pb1-C1-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O5 77.3(1) F: 0.5 - x, 1.5 - y, 1.5 - z F: 0.5 - x, 1.5 - y, 1.5 - z F: 0.5 - x, 1.5 - y, 1.5 - z F: 0.5 - x, 1.5 - y, 1.5 - z F: 0.5 - x, 1.5 - y, 1.5 - z F: 0.		Pb1-N6	2.912(2)	Pb1-N6	2.836(3)	Pb1-N6	2.711(4)	Pb1-O5	2.809(4)
Seperation C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-I2 93.66(2) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-01 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-03 76.7(1) C11-Pb1-C11 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-11 ⁱ 81.12(1) N1-Pb1-05 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-11-Pb ⁱ 98.88(1) N1-Pb1-05 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-11-Pb ⁱ 98.88(1) N1-Pb1-05 79.2(1) Pb1-05 7.3(1) Y Y Y Y Y Y Y Y Y Y Y <td>C[1-Pb1-Cl2 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-L2 93.66(2) N1-Pb1-N2 63.2(1) C[1-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) Cl1-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) Cl1-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O3 76.7(1) Cl1-Pb1-Cl1ⁱ 79.64(2) Br1-Pb1-Br1ⁱ 81.09(1) I1-Pb1-N1 88.8(1) N1-Pb1-O5 79.2(1) Pb1-Cl1-Pb1ⁱ 100.36(2) Pb1-Br1-Pb1ⁱ 81.09(1) I1-Pb1-Iⁱ 88.8(1) N1-Pb1-O6 104.1(1) O1-Pb1-O3 45.9(1) O1-Pb1-O3 45.9(1) O1-Pb1-O5 77.3(1)</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>Pb1-O6</td> <td>2.691(6)</td>	C [1-Pb1-Cl2 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-L2 93.66(2) N1-Pb1-N2 63.2(1) C [1-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) Cl1-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) Cl1-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O3 76.7(1) Cl1-Pb1-Cl1 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-N1 88.8(1) N1-Pb1-O5 79.2(1) Pb1-Cl1-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 81.09(1) I1-Pb1-I ⁱ 88.8(1) N1-Pb1-O6 104.1(1) O1-Pb1-O3 45.9(1) O1-Pb1-O3 45.9(1) O1-Pb1-O5 77.3(1)								Pb1-O6	2.691(6)
 C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-I2 93.66(2) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 I43.47(5) Br1-Pb1-N2 I43.34(6) I1-Pb1-N2 I39.93(9) N1-Pb1-N6 I05.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 I34.17(5) Br1-Pb1-N6 I34.09(6) I1-Pb1-N5 85.03(9) N1-Pb1-O3 76.7(1)	C11-Pb1-C12 92.44(2) Br1-Pb1-Br2 92.77(2) I1-Pb1-12 93.66(2) N1-Pb1-N2 63.2(1) C11-Pb1-N1 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) C11-Pb1-C11 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-I1 ⁱ 81.12(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O5 77.3(1) i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z									
Solution 86.79(5) Br1-Pb1-N1 86.74(7) I1-Pb1-N1 85.7(1) N1-Pb1-N5 156.7(1) C11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) C11-Pb1-Cl1 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-I1 ⁱ 81.12(1) N1-Pb1-O5 79.2(1) Pb1-Cl1-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O5 79.2(1) Pb1-Cl1-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O5 77.3(1) i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5	⁶ ⁷ ⁷		Cl1-Pb1-Cl2	92.44(2)	Br1-Pb1-Br2	92.77(2)	I1-Pb1-I2	93.66(2)	N1-Pb1-N2	63.2(1)
Solution C(11-Pb1-N2 143.47(5) Br1-Pb1-N2 143.34(6) I1-Pb1-N2 139.93(9) N1-Pb1-N6 105.6(1) C(11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C(11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) C(11-Pb1-CI1 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-I1 ⁱ 81.12(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O6 104.1(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O6 104.1(1) O1-Pb1-O3 45.9(1) O1-Pb1-O5 77.3(1) 77.3(1) i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z	⁸ Difference (11-Pb1-N2) (143.47(5) Br1-Pb1-N2) (143.34(6) I1-Pb1-N5) (11-Pb1-N5) (11-Pb1-N6) (134.07(5) Br1-Pb1-N6) (11-Pb1-N6) (138.3(1) N1-Pb1-O3 76.7(1) (11-Pb1-C11) (1-Pb1-C11) (100.36(2) Pb1-Br1-Pb1 (98.91(2) Pb1-I1-Pb (98.88(1) N1-Pb1-O6 (104.1(1) (01-Pb1-O3 (01-Pb1-O3 45.9(1) (01-Pb1-O3 77.3(1) (11-Pb1-N5 (11-P		Cl1-Pb1-N1	86.79(5)	Br1-Pb1-N1	86.74(7)	I1-Pb1-N1	85.7(1)	N1-Pb1-N5	156.7(1)
Solution Cl1-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) Cl1-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) Cl1-Pb1-Cl1 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-I1 ⁱ 81.12(1) N1-Pb1-O5 79.2(1) Pb1-Cl1-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O6 104.1(1) O1-Pb1-O3 45.9(1) 01-Pb1-O5 77.3(1)	C11-Pb1-N5 84.69(5) Br1-Pb1-N5 83.75(6) I1-Pb1-N5 85.03(9) N1-Pb1-O1 80.2(1) C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) C11-Pb1-C11 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-I1 ⁱ 81.12(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O6 104.1(1) O1-Pb1-O5 .		Cl1-Pb1-N2	143.47(5)	Br1-Pb1-N2	143.34(6)	I1-Pb1-N2	139.93(9)	N1-Pb1-N6	105.6(1)
Det C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) C11-Pb1-C11 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-I1 ⁱ 81.12(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O6 104.1(1) O1-Pb1-O3 45.9(1) 01-Pb1-O5 77.3(1) i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z	Product C11-Pb1-N6 134.17(5) Br1-Pb1-N6 134.09(6) I1-Pb1-N6 138.3(1) N1-Pb1-O3 76.7(1) C11-Pb1-C11 ⁱ 79.64(2) Br1-Pb1-Br1 ⁱ 81.09(1) I1-Pb1-I1 ⁱ 81.12(1) N1-Pb1-O5 79.2(1) Pb1-C11-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O6 104.1(1) O1-Pb1-O3 45.9(1) 01-Pb1-O5 77.3(1) i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z i: 0.5 - x, 1.5 - y, 1.5 - z	s	Cl1-Pb1-N5	84.69(5)	Br1-Pb1-N5	83.75(6)	I1-Pb1-N5	85.03(9)	N1-Pb1-O1	80.2(1)
C11−Pb1−Cl1 ⁱ 79.64(2) Br1−Pb1−Br1 ⁱ 81.09(1) I1−Pb1−I1 ⁱ 81.12(1) N1−Pb1−O5 79.2(1) Pb1−Cl1−Pb1 ⁱ 100.36(2) Pb1−Br1−Pb1 ⁱ 98.91(2) Pb1−I1−Pb ⁱ 98.88(1) N1−Pb1−O6 104.1(1) O1−Pb1−O3 45.9(1) O1−Pb1−O5 77.3(1) i: 0.5 − x, 1.5 − y, 1.5 − z	C11−Pb1−C11 ⁱ 79.64(2) Br1−Pb1−Br1 ⁱ 81.09(1) I1−Pb1−I1 ⁱ 81.12(1) N1−Pb1−O5 79.2(1) Pb1−C11−Pb1 ⁱ 100.36(2) Pb1−Br1−Pb1 ⁱ 98.91(2) Pb1−I1−Pb ⁱ 98.88(1) N1−Pb1−O6 104.1(1) O1−Pb1−O3 45.9(1) O1−Pb1−O5 77.3(1) i: 0.5 − x, 1.5 − y, 1.5 − z	ngle	Cl1-Pb1-N6	134.17(5)	Br1-Pb1-N6	134.09(6)	I1-Pb1-N6	138.3(1)	N1-Pb1-O3	76.7(1)
Pb1-Cl1-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O6 104.1(1) O1-Pb1-O3 45.9(1) O1-Pb1-O5 77.3(1)	Pb1-Cl1-Pb1 ⁱ 100.36(2) Pb1-Br1-Pb1 ⁱ 98.91(2) Pb1-I1-Pb ⁱ 98.88(1) N1-Pb1-O6 104.1(1) O1-Pb1-O3 45.9(1) O1-Pb1-O5 77.3(1)	Ā	$Cl1-Pb1-Cl1^i$	79.64(2)	Br1–Pb1–Br1 ^{<i>i</i>}	81.09(1)	I1–Pb1–I1 ^{<i>i</i>}	81.12(1)	N1-Pb1-O5	79.2(1)
i: 0.5 - x, 1.5 - y, 1.5 - z	01-Pb1-O3 45.9(1) 01-Pb1-O5 77.3(1)		$Pb1-Cl1-Pb1^{i}$	100.36(2)	Pb1–Br1–Pb1 ⁱ	98.91(2)	Pb1–I1–Pb ⁱ	98.88(1)	N1-Pb1-O6	104.1(1)
i: 0.5 - x, 1.5 - y, 1.5 - z	i: 0.5 - x, 1.5 - y, 1.5 - z								O1-Pb1-O3	45.9(1)
i: 0.5 - x, 1.5 - y, 1.5 - z	i: 0.5 - x, 1.5 - y, 1.5 - z								O1-Pb1-O5	77.3(1)
			0							
			6							
			0							

Table 2. Selected bond lengths (Å) and angles (°) for complexes 1-4 with estimated standard deviations in parentheses.

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	D−H···A	<i>d</i> (D–H)	$d(H \cdots A)$	<(DHA)	$d(D\cdots A)$	Symmetry code on A atom
1	$C(1)-H(1)\cdots Cl(1)$	0.949	2.823	137.0	3.576(3)	0.5 - x, 1.5 - y, 1.5 - z
	$C(2)-H(2)\cdots Cl(2)$	0.951	2.7239	132.6	3.439(3)	1 - x, $0.5 + y$, $1.5 - z$
	C(7) - H(7) - N(7)	0.951	2.433	134.6	3.227(3)	0.5 - x, y, 1 - z
	C(21)-H(21)····N(3)	0.950	2.465	133.6	3.195(3)	0.5 - x, y, 1 - z
	$C(26)-H(26)\cdots Cl(1)$	0.950	2.8390	163.4	3.759(3)	-0.5 + x, -0.5 + y, -0.5 + z
2	$C(1)-H(1) \cdots Br(1)$	0.940	2.926	138.3	3.681(3)	0.5 - x, 1.5 - y, 1.5 - z
	$C(2)-H(2)\cdots Br(2)$	0.941	2.8671	134.1	3.587(4)	1 - x, $0.5 + y$, $1.5 - z$
	C(12)-H(12)- Br(2)	0.940	3.0338	133.8	3.746(5)	1 - x, 2 - y, 1 - z
	C(7)-H(7)… N(7)	0.940	2.543	134.2	3.269(5)	0.5 - x, y, 1 - z
	C(21)-H(21) N(3)	0.941	2.516	133.5	3.237(5)	0.5 - x, y, 1 - z
	C(26)-H(26)-Br(1)	0.940	2.8809	163.7	3.792(5)	-0.5 + x, $-0.5 + y$, $-0.5 + z$
3	$C(1)-H(1)\cdots I(1)$	0.940	3.0955	138.7	3.852(7)	0.5 - x, 1.5 - y, 1.5 - z
	C(2) - H(2) - I(2)	0.938	3.1777	140.5	3.947(7)	1 - x, 0.5 + y, 1.5 - z
	$C(7) - H(7) \cdots N(7)$	0.940	2.549	137.4	3.303(7)	0.5 - x, y, 1 - z
	C(21)-H(21) N(3)	0.938	2.689	134.4	3.411(7)	0.5 - x, y, 1 - z
	C(26)-H(26)…I(1)	0.940	3.0121	151.8	3.866(7)	-0.5 + x, -0.5 + y, -0.5 + z
1	C(1) - H(1) - O(1)	0.950	2 544	138.2	3 312(6)	X N 7
Ŧ	C(1) = H(1) = U(1)	0.950	2.544	150.2	3.312(0) 3.414(7)	x, y, z
	C(10) = H(10) = O(3) C(18) = H(18) = O(3)	0.949	2.520	137.1	3.414(7)	x, 1 + y, z 1 - r 1 - v - z
	C(18) = H(18) = O(3)	0.950	2.565	126.7	3.204(0) 3.205(7)	1 x, 1 y, z 1 - x, 1 - y, -z
	C(18) = H(18) = O(2) C(28) = H(28) = O(1)	0.930	2.030	135.1	3.393(7)	1 - x, 1 - y, -z
	$C(28) \Pi(28) \Pi(01)$ $C(24) = \Pi(24) \dots O(2)$	0.950	2.032	120.5	3.260(7)	$1 \lambda, 1 y, \zeta$
	C(24) = H(24) = H(2)	0.930	2.571	147.0	3.214(7)	-1 + x, y, z
	$C(2) \Pi(2) \cdots O(4)$ $C(4) = \Pi(4) \cdots O(5)$	0.950	2.404	155.0	3.170(0)	$\begin{array}{c} x, 1 + y, z \\ 1 - x - y, 1 - z \end{array}$
	$C(4) = \Pi(4) = \Pi(0(3))$ $C(14) = \Pi(14) = \Pi(0(5))$	0.951	2.575	157.5	3.470(0) 2.204(7)	1 - x, -y, 1 - z
	C(14) = H(14) = O(3) C(10) = H(10) = O(4)	0.950	2.514	134.1	3.374(7)	1 x, y, 1-z
	$C(10) \Pi(10)^{-10}O(4)$	0.950	2.337	129.9	3.249(7)	1 + x, y, z
	C(7) = H(7) =	0.930	2.432	149.3	3.287(7)	$-1 + \lambda, y, \lambda$
	\mathbf{O}					

Table 3. Hydrogen bonds dimensions (Å and °) in complexes 1–4.

Table 4. NBO analysis results for the PPTA ligand and its dinuclear $1^{opt}-3^{opt}$ isolated complexes. Values are the average of charge (AVG) on similar atoms (N atom labels according to Scheme 1).

		Carbon ^{AVG}	Hydrogen ^{AVG}	N1	N2	N3	N4	Halide	Metal	
PI	ρτα [-0.0591	0.2281	-0.2111	-0.2940	_0 4798	-0.4687		_	×
11	1 ^{opt}	-0.0501	0.2294	-0.1781	-0.3055	-0.5160	-0.5307	-0.6942	1.2637	
2	2 ^{opt}	-0.0491	0.2298	-0.1678	-0.3263	-0.5146	-0.5434	-0.6649	1.1814	
3	3 ^{opt}	-0.0478	0.2304	-0.1671	-0.3339	-0.5162	-0.5374	-0.6276	1.0891	



Table 5. HOHO and LUMO orbitals for the optimized structures $1^{opt}-3^{opt}$.

Figure Captions

- Scheme 1. 5-Phenyl-3-(pyridin-2-yl)-1,2,4-triazine (PPTA).
- Scheme 2. Coordination modes of 3-(pyridin-2-yl)-1,2,4-triazine-based ligands.
- Scheme 3. The CSD average of bond lengths and angles for complexes with the PbN₄O₄ environment.
- Figure 1. ORTEP diagram of the molecular structure of **1**. The ellipsoids are drawn at the 35% probability level.
- Figure 2. Distorted capped octahedral geometry around the lead atom in the crystal structure of **1**.
- Figure 3. ORTEP diagram of the molecular structure of **4**. The ellipsoids are drawn at the 35% probability level.

Figure 4. Distorted cube geometry around the lead atom in the crystal structure of 4.

- Figure 5. Pie chart, the percentage of different coordination modes of nitrate ion among the complexes of lead.
- Figure 6. Packing of **3**, showing hydrogen bonds. Each PbN₄I₃ unit is shown as a distorted capped octahedron. Only the hydrogen atoms involved in hydrogen bonding are shown.
- Figure 7. Packing of **4**, showing the hydrogen bonds. Each PbN₄O₄ unit is shown as a distorted cube. Only the hydrogen atoms involved in hydrogen bonding are shown.
- Figure 8. Theoretical study (DFT) of the effect of the dihedral angle variation between pyridine and triazine rings on the energy level of one isolated PPTA ligand.

























Synopsis

Four complexes of 5-phenyl-3-(pyridin-2-yl)-1,2,4-triazine (PPTA) including, namely $[Cl(PPTA)_2Pb(\mu-Cl)_2Pb(PPTA)_2Cl]$, $[Br(PPTA)_2Pb(\mu-Br)_2Pb(PPTA)_2Br]$, $[I(PPTA)_2Pb(\mu-I)_2Pb(PPTA)_2I]$ and $[(PPTA)_2Pb(NO_3)_2]$, were prepared and their spectral and structural properties were investigated. The experimental data are compared with the Cambridge Structural Database and theoretical results.