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Pb···N interactions and π -stacking in lead(II) bis(hydrazone) compounds



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ABSTRACT

2,6-Diacetylpyridine-*bis*(benzoylhydrazone), H_2L^{Ph} , reacts with Pb(OAc)₂·3H₂O and NEt₃ as a supporting base forming a polymeric solid of the composition [Pb(L^{Ph})]_n. A reaction with pyridine results in cleavage of the polymer and formation of the dimeric, crystalline compound [Pb(py)(L^{Ph})]₂.

Similar reactions with PbX₂ salts (X = Cl, Br, I) also give almost insoluble solids of the tentative composition [Pb(H₂L^{Ph})X₂]_n. After ongoing reactions with DMSO, single deprotonation of the organic ligand and the formation of pseudo-dimeric [Pb(HL^{Ph})X]₂ complexes was observed. Depending on the presence of solvent molecules they form different supramolecular aggregates by π - π interactions.

The use of $Pb(NO_3)_2$ results in a dimeric structure with relatively short Pb–O bonds of 2.442(2) Å between the monomeric sub-units. The formed dimers aggregate to a polymeric assembly by hydrogen bonds.

The products were studied by spectroscopic methods and X-ray diffraction.

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1. Introduction

The structural coordination chemistry of 2,6-diacetylpyridinebis(hydrazones), -bis(semicarbazones) or -bis(thiosemi-carbazones) with lead(II) is hitherto restricted to syn close complexes [1–5]. The compounds are formed by N_3O_2 or N_3S_2 coordination of the pentadentate ligands as is shown in Chart 1. While there is only each one structurally characterized example for hydrazone complexes I and semicarbazone complexes II [1,4], a few thiosemicarbazone compounds of type III are reported [2,3,5]. The lead(II) compounds are usually obtained by electrochemical syntheses [1,2], conventional metathesis procedures [3,4] or by decomposition of methyllead(IV) compounds [5].

Intermolecular Pb···S and π - π interactions as well as N-H···S or N-H···N hydrogen bonds have been described for the lead(II) thiosemicarbazonato complexes (type III) [2,3,5]. For the structurally studied lead(II) hydrazonato and semicarbazone complexes there are no related intermolecular interactions [1,4].

2,6-Diacetylpyridine-*bis*(benzoylhydrazone) can coordinate as a neutral, monoanionic or dianionic ligand. The degree of deprotonation in the products is influenced by the coordinated metal ion, the reactions conditions and the availability of potential anionic coligands or counter ions [6,7]. A considerable number of mononu-

* Corresponding author. *E-mail address:* vaniaschwade@ufgd.edu.br (V.D. Schwade). clear and dinuclear structures involving the first row transition metals have been prepared and structurally characterized. With the *p* block metals, however, there are only a few examples with Sn(II), Sb(III) and Bi(III) ions [1,8] in addition to the Pb(II) compounds referred above and shown in Chart 1. The coordination spheres of the metal ions are completed by anions such as halides or nitrate, and by solvent molecules such as water, dimethyl sulfoxide, dimethylformamide or pyridine. The coordination of two ligand molecules to the same metal ion is found only in Ln^{3+} and Th^{4+} complexes [7–11], for which large coordination numbers are common.

In the present communication, we describe syntheses and crystal structures of pseudo-dimeric and polymeric lead(II) complexes with 2,6-diacetylpyridine-*bis*(benzoylhydrazone) (H_2L^{Ph}) and the influence of solvent molecules and anionic co-ligands in the structural chemistry of this class of componds.





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Chart 1. Benzoylhydrazone, semicarbazone and thiosemicarbazone complexes of Pb(II).

2. Results and discussion

2.1. $[Pb(L^{Ph})]_n$ and $[Pb(py)(L^{Ph})]_2$

Equivalent amounts of lead(II) acetate and H_2L^{Ph} react after addition of triethylamine as supporting base in methanol with a yellow solid being formed. The product precipitates directly from the reaction mixture in a practically quantitative yield. It is only very slightly soluble in dimethylformamide or dimethylsulfoxide, even under gentle heating, but well soluble in pyridine. Thus, recrystallization from a pyridine/methanol mixture gives yellow crystals of [Pb(py)(L^{Ph})]₂ (Scheme 1).

rcrystalls of $[Pb(py)(L^{Ph})]_2$ (Scheme 1). The IR spectrum of $[Pb(L^{Ph})]_n$ clearly supports the coordination of the dianionic $[L^{Ph}]^{2-}$ ligand by the observed bathochromic shift of the $v_{C=0}$ frequency from 1663 cm⁻¹ in H₂L^{Ph} to 1497 cm⁻¹ in the product, while the v_{N-H} vibrations disappeared in the spectrum of the complex. Unfortunately, the compound was not sufficiently soluble to obtain NMR spectra of reasonable quality. A polymeric structure as is depicted in Scheme 1 is proposed for this compound (i) by its low solubility, even in a number of coordinating solvents, and (ii) by the assumption of a stereochemically active lone-pair in the coordination plane of the chelating ligands, which would allow polymerization perpendicular to this plane, e.g. by π -stacking or weak Pb···N interaction as they have been found in the pyridine derivative, the structure of which will be discussed *vide infra*.

The IR spectrum of the pyridine adduct $[Pb(py)(L^{Ph})]_2$ shows the presence of pyridine by the bands at 1450, 1216, 767 and 621 cm⁻¹, which additionally appear in comparison to the spectrum of the polymeric starting material $[Pb(L^{Ph})]_n$.

 $[Pb(py)(L^{ph})]_2$ crystallizes in the orthorhombic space group Pbca. Fig. 1a depicts an ellipsoid plot of its molecular structure and selected bond lengths and angles are summarized in Table 1. The gap in the coordination sphere, which can be assigned to the position of the stereochemically active lone-pair of the Pb(II) ion, can best be seen in Fig. 1b. The corresponding O1–Pb1–O2 angle of 104.21(6)° is clearly larger than the O–N and N–N angles inside the plane, which range between 60.16(6)° and 63.57(7)°. The pyridine ligand is coordinated in the apical position and completes the



Fig. 1. (a) Ellipsoid representation [33] of the monomeric unit of the molecular structure of $[Pb(py)(HL^{Ph})]_2$. Thermal ellipsoids represent 50 per cent probability. Hydrogen atoms have been omitted for clarity. (b) Representation of the pseudo-dimeric structure formed by Pb…N interactions. Symmetry operator: (') –*x*, –*y* + 1, –*z* + 1.



Scheme 1. Formation of $[Pb(py)(L^{Ph})]_2$ from $[Pb(L^{Ph})]_n$.

| Table 1 |
|--|
| Selected bond lengths (Å) and angles (°) in $[Pb(py)(L^{Ph})]_2$. |

| Pb1-01 | 2.6174(19) | 01-C8 | 1.245(3) | Pb1···N3′ | 3.180(2) |
|-----------|------------|-----------|-----------|-----------|-----------|
| Pb1-O2 | 2.4794(19) | N3-C8 | 1.346(3) | | |
| Pb1–N1 | 2.5545(19) | N2-N3 | 1.377(3) | | |
| Pb1–N2 | 2.603(2) | O2-C17 | 1.273(3) | | |
| Pb1-N4 | 2.514(2) | N5-C17 | 1.331(3) | | |
| Pb1-N6 | 2.518(2) | N4-N5 | 1.375(3) | | |
| 01-Pb1-N1 | 120.63(7) | O2-Pb1-N1 | 125.18(6) | N1-Pb1-N4 | 63.57(7) |
| 01-Pb1-N2 | 60.16(6) | O2-Pb1-N2 | 158.67(7) | N1-Pb1-N6 | 79.37(7) |
| 01-Pb1-N4 | 156.50(7) | O2-Pb1-N4 | 62.93(6) | N2-Pb1-N4 | 125.38(6) |
| 01-Pb1-N6 | 78.41(7) | O2-Pb1-N6 | 80.64(7) | N2-Pb1-N6 | 81.83(7) |
| 01-Pb1-02 | 104.21(6) | N1-Pb1-N2 | 62.61(7) | N4-Pb1-N6 | 80.00(7) |
| | | | | | |

Symmetry operator: (') -x, -y + 1, -z + 1.



Scheme 2. Formation of [Pb(HL^{Ph})X]₂.

pentagonal pyramidal coordination sphere of the lead(II) ion. The pentagonal N_3O_2 plane shows only slight deviations from planarity (a maximum deviation of 0.078(1) Å has been found for the atom N2). The metal atom is situated 0.4432(9) Å below this plane, in the opposite direction of the pyridine ligand.

 $[Pb(py)(L^{Ph})]_2$ is the first neutral complex with a bis(hydrazonato) ligand having a neutral ligand in the apical position. In the literature, we only have found one structurally related compound with a cyanido ligand in the apical position [1].

The Pb–O bond lenghts are different, with the Pb1–O1 bond of 2.6174(19) Å being markedly longer than the Pb1–O2 one (2.4794(19) Å). This effect may be caused by the intermolecular Pb1…N3' interactions.

Intermolecular interactions between the monomers originate a pseudo-dimeric structure (Fig. 1b). The Pb1 \cdots N3' distance of 3.180 (2) Å (symmetry code: -x, -y + 1, -z + 1) is within the sum of the *van der Waals* radii [12] of the corresponding atoms and is in the average of Pb \cdots N interactions found before for isonicotinoylhydrazone derivatives [13,14].

Finally, two points are remarkable: (i) only the excellent donor pyridine was able to break the polymeric structure of [Pb(py) (L^{Ph})]₂, while the compound did not react in the same way with DMSO or DMF, and (ii) that the fragmentation of the polymer stops in the reported pseudo-dimeric arrangement and does not give the (more expected) bis pyridine adduct. The latter fact might be due to the *lone pair* effect, which rules the coordination chemistry of lead(II) compounds [15,16]. The coordination of a second molecule of pyridine and the formation of pentagonal bipyramidal coordination spheres has been observed for corresponding Mn(II), Co(II) and Cd(II) compounds [17,18].

2.2. $[Pb(H_2L^{Ph})X_2]_n$ and $[Pb(HL^{Ph})X]_2$ (X = Cl, Br, I)

Reactions of lead(II) halides with H_2L^{Ph} in methanol, but without the addition of a supporting base also result in the formation of



Fig. 2. (a) Ellipsoid representation [33] of the molecular structure of $[Pb(HL^{Ph})Cl]_2$. Thermal ellipsoids represent 50 per cent probability. Hydrogen atoms have been omitted for clarity, with exception of NH. (b) View of the pseudo-dimeric structure formed by π - π and Pb \cdots N interactions. Symmetry operator: (') –x + 1, –y + 1, –z + 1.

sparingly soluble, yellow to orange-yellow solids (Scheme 2). They can be assigned to a composition of $[Pb(H_2L^{Ph})X_2]_n$ (X = Cl, Br, I) by means of elemental analysis and their IR spectra. The compounds are most probably polymers with infinite

| Table 2 |
|--|
| Selected bond lengths (Å) and angles (deg) in [Pb(HLPh)X]2 complexes |

| | [Pb(HL ^{Ph})Cl] ₂ | [Pb(HL ^{Ph})Br] ₂ | $[Pb(HL^{Ph})I]_2$ | $[Pb(HL^{Ph})I]_2 \cdot 2MeOH \cdot H_2O$ |
|-----------|--|--|--------------------|---|
| Pb1-01 | 2.465(3) | 2.459(3) | 2.4503(19) | 2.512(6) |
| Pb1-O2 | 2.924(4) | 2.919(4) | 2.927(3) | 2.851(7) |
| Pb1-N1 | 2.556(4) | 2.553(3) | 2.566(2) | 2.590(7) |
| Pb1–N2 | 2.460(4) | 2.448(3) | 2.439(2) | 2.492(6) |
| Pb1–N4 | 2.786(4) | 2.809(4) | 2.820(2) | 2.738(7) |
| Pb1-X1 | 2.6258(17) | 2.7750(5) | 2.9950(3) | 2.9879(7) |
| Pb1···N3′ | 3.156(4) | 3.170(3) | 3.180(2) | 3.190(7) |
| 01-C8 | 1.263(5) | 1.263(4) | 1.266(3) | 1.272(10) |
| N3-C8 | 1.331(6) | 1.339(5) | 1.335(4) | 1.322(10) |
| N2-N3 | 1.390(5) | 1.382(4) | 1.381(3) | 1.372(9) |
| 02-C17 | 1.188(6) | 1.211(5) | 1.213(4) | 1.237(11) |
| N5-C17 | 1.379(7) | 1.359(5) | 1.360(4) | 1.315(11) |
| N4-N5 | 1.379(5) | 1.383(4) | 1.383(3) | 1.368(9) |
| 01-Pb1-N1 | 127.71(12) | 128.29(9) | 129.06(7) | 126.3(2) |
| 01-Pb1-N2 | 64.39(12) | 64.41(10) | 65.21(7) | 62.9(2) |
| 01-Pb1-N4 | 164.90(12) | 165.25(9) | 165.04(6) | 166.0(2) |
| 01-Pb1-X1 | 82.43(10) | 82.67(7) | 82.33(5) | 87.05(16) |
| 01-Pb1-02 | 117.05(12) | 116.86(10) | 115.97(7) | 115.9(2) |
| O2-Pb1-N1 | 114.94(13) | 114.66(11) | 114.68(8) | 117.1(2) |
| 02-Pb1-N2 | 170.23(13) | 170.15(11) | 171.92(8) | 177.9(2) |
| 02-Pb1-N4 | 55.50(12) | 55.24(10) | 55.37(7) | 57.3(2) |
| O2-Pb1-X1 | 98.49(9) | 100.73(8) | 101.92(6) | 86.63(15) |
| N1-Pb1-N2 | 65.39(13) | 65.41(10) | 65.48(7) | 64.4(2) |
| N1-Pb1-N4 | 60.13(12) | 60.16(10) | 59.85(7) | 60.0(2) |
| N1-Pb1-X1 | 85.04(10) | 83.90(7) | 82.48(5) | 87.95(15) |
| N2-Pb1-N4 | 125.50(13) | 125.55(10) | 125.32(7) | 124.3(2) |
| N2-Pb1-X1 | 91.26(10) | 89.10(8) | 86.14(5) | 94.95(16) |
| N4-Pb1-X1 | 85.78(11) | 86.70(7) | 87.65(5) | 80.44(15) |

Symmetry operator: (') -x + 1, -y + 1, -z + 1 for $[Pb(HL^{Ph})Cl]_2$ and $[Pb(HL^{Ph})l]_2$; -x + 2, -y, -z + 2 for $[Pb(HL^{Ph})Br]_2$.



Fig. 3. Polymeric structure of $[Pb(HL^{Ph})I]_2$ ·2MeOH·H₂O formed by π -stacking interactions between the pyridine and phenyl rings [33]. The solvent molecules have been omitted.

···Cl-Pb(HL^{Ph})-Cl-Pb(HL^{Ph})-Cl··· chains. The formation of bis(chlorido)-bridged dimers as shown in parenthesis in Scheme 2 cannot be ruled out, but may be regarded as unlikely, since such a coordination would require a holodirected, stereochemically inactice 6s lone pair, while for all other compounds of this study and in the previously reported lead(II) complexes with 2,6-diacetylpyridine-*bis*(hydrazones) or *-bis*(semicarba-zones) hemidirected lone pairs were observed.

Evidence for the coordination of H_2L^{Ph} in protonated form is clearly given by the IR spectra of the compounds. The v_{NH} vibrations appear at 3143, 3351 and 3367 cm⁻¹ for the compounds with Cl, Br and I, respectively. More indicative is the detection of the $v_{C=0}$ frequencies at 1641, 1654 and 1657 cm⁻¹ for these compounds, which is a strong indicator, that almost no delocalization of electron density is present in the corresponding chelate rings. This contrasts the situation in complexes with deprotonated benzoyl-hydrazones, where the corresponding IR bands are bathochromically shifted by more than 100 cm⁻¹. Interestingly, the spectroscopic results are not reflected by the bond lengths of the C–O bonds in the dimeric units isolated from the polymers $[Pb(L^{Ph})]_n$ and $[Pb(H_2L^{Ph})X_2]_n$. Dissolution of $[Pb(H_2L^{Ph})X_2]_n$ compounds in DMSO results in the

Dissolution of $[Pb(H_2L^{Ph})X_2]_n$ compounds in DMSO results in the scission of the polymeric chains and the formation of pseudodimeric complexes of the composition $[Pb(HL^{Ph})X]_2$ (X = Cl, Br, I). Remarkably, these reactions go along with abstraction of one equivalent of HX and the formation of single-deprotonated $[HL^{Ph}]^-$ ligands. Coordination of H_2L^{Ph} and its derivatives as neutral ligands to M^{2+} ions has been observed before for Mn, Fe, Co, Ni, Cu, Zn and Cd in structurally well-characterized mononuclear complexes [19–25]. For the deprotonation of coordinated 2,6-diacetylpyridine-*bis*(hydrazone) ligands, there is to the best of our knowledge only one precedent. It has been observed for structurally related $[M(H_2L)Cl_2]$ complexes (M = Mn, Co) after the addition of sodium tetraphenylborate [26].

The [Pb(HL^{Ph})X]₂ complexes are sufficiently soluble in DMSO to record ¹H NMR spectra of reasonable quality. The NH signals can be detected at 10.87, 11.05 and 11.47 ppm for [Pb(HL^{Ph})Cl]₂, [Pb(HL^{Ph}) Br]₂ and [Pb(HL^{Ph})I]₂, respectively. Monodeprotonation of the organic ligands can also been derived from the IR spectra of the complexes, where each pairs of signals are observed in the region around 1670 and 1507 cm⁻¹. The v_{NH} vibrations appear at 3242, 3262 and 3265 cm⁻¹ for [Pb(HL^{Ph})Cl]₂, [Pb(HL^{Ph})Br]₂ and [Pb(HL^{Ph}) I]₂, respectively.

[Pb(HL^{Ph})Cl]₂, [Pb(HL^{Ph})Br]₂ and [Pb(HL^{Ph})I]₂ are isostructural and crystallize in the monoclinic space group $P2_1/c$. Fig. 2a depicts an ellipsoid plot of [Pb(HL^{Ph})Cl]₂ as a representative of the halide compounds. The molecular structures of [Pb(HL^{Ph})Br]₂ and [Pb(HL^{Ph})I]₂ are virtually identical. For this reason no extra figures are given for them. Selected bond lengths and angles of all three [Pb(HL^{Ph})X]₂ complexes are summarized in Table 2, the corresponding labeling scheme has been adopted from Fig. 2a. By means of the Pb-O distances (each one in the range of 2.4-2.5 Å and one between 2.8 and 2.9 Å) it is possible to distinguish between the "protonated" and the "deprotonated arms" of the ligands indicating a weaker bonding to the uncharged carbonyl oxygen atoms O2. The Pb-Cl bond length in the chloride compound of 2.626(2) Å is remarkably shorter than the distance of 2.707(4) Å, which has been determined for the related semicarbazone complex reported in Ref. [4]. There are no reference values available for the Pb-Br and Pb-I bonds in [Pb(HL^{Ph})Br]₂ and [Pb(HL^{Ph})I]₂, since they represent the first lead(II) hydrazone complexes with these halides as co-ligands.

The pentagonal N_3O_2 coordination spheres of the halide complexes are almost planar. Maximum deviations from planarity was found for the atoms N2 or N4 for all complexes and are in the range between 0.161(5) and 0.281(3) Å. The lead atoms are situated out of these mean least-square planes on the opposite sides compared to the halide ligands with distances between 0.026(2) and 0.119(3) Å.

Intermolecular interactions between the monomers produce pseudo-dimeric structures, as can be seen in Fig. 2b. Since the main structural features are identical for [Pb(HL^{Ph})Cl]₂, [Pb(HL^{Ph})Br]₂ and [Pb(HL^{Ph})I]₂, the situation in the chlorido compound shall be described exemplarily. Weak Pb1···N3' (symmetry code: -x + 1, -y + 1, -z + 1) interactions organize each two of the molecules parallel to each other with Pb-N distances of 3.156(4) Å (3.170 (3) Å for the bromido complex and 3.180(2) Å for the iodido complex). The Pb \cdots N interactions are reinforced by π - π interactions between the pyridine rings and the phenyl rings of the adjacent molecule. The 'parallel offset' aromatic stacking arrangement [27] is identified in these complexes. The centroid-centroid distances are 3.653, 3.651 and 3.654 Å for [Pb(HLPh)Cl]₂, [Pb(HLPh)Br]₂ and [Pb(HL^{Ph})I]₂, respectively. To the best of our knowledge, there is only one more report, which describes both interactions (Pb...N and $\pi - \pi$) in a lead(II) compound with a monohydrazonato ligand, and a copper(II) compound with 2-pyridylaldehyde isonicotinoylhydrazone [28].

Since the solvated iodide derivative $[Pb(HL^{Ph})I]_2 \cdot 2MeOH \cdot H_2O$ crystallizes with solvent molecule in the monoclinic space group $P2_1/n$, the crystal packing features of this compound are different from the not solvated halido complexes. Also here, relatively short intermolecular Pb...N distance is observed. With 3.190(7) Å they are slightly longer than for the previous halido compounds. Consequently, the centroid–centroid distance of the π -stacking interactions is also bigger (3.744 Å). The pseudo-dimer formed due to these interactions is shown in Fig. 3. In contrast to the situation in $[Pb(HL^{Ph})X]_2$, the phenyl rings, which are not involved in π -stacking to form the pseudo-dimers establish a second group

of π - π -interactions organizing the dimers into a two-dimensional network along the (001) plane. The centroid–centroid distances of these weak interactions are 3.763 and 3.899 Å. The assembly of the pseudo-dimers into a supramolecular 2D network is depicted in Fig. 3.

2.3. [Pb(HL^{Ph})(NO₃)]₂

The reaction of H_2L^{Ph} with lead(II) nitrate in methanol forms without the adddition of a supporting base immediately a slightly



Fig. 4. (a) Ellipsoid representation [33] of the asymmetric unit of $[Pb(HL^{Ph})(NO_3)]_2$. Thermal ellipsoids represent 50 per cent probability. Hydrogen atoms have been omitted for clarity, with exception of NH. (b) View of the dimeric molecular structure. (c) Polymeric network formed by N–H···O hydrogen bonds. Phenyl groups have been omitted for clarity. Symmetry operators: (') –*x*, –*y* + 1, –*z*; ('') –*x* + 0.5, *y* – 0.5, –*z* + 0.5.

| Table 3 |
|--|
| Selected bond lengths (Å) and angles (°) in [Pb(HL ^{Ph})(NO ₃)] ₂ . |

| Pb1-O1 | 2.7513(19) | O1-C8 | 1.227(3) | Pb1···O2′ | 2.4420(16) |
|---------------------------|------------------|-----------|-----------|------------|------------|
| Pb1-O2 | 2.7082(15) | N3-C8 | 1.359(3) | Pb1···O5 | 3.309(2) |
| Pb1-N1 | 2.5431(17) | N2-N3 | 1.372(2) | | |
| Pb1-N2 | 2.6693(17) | 02-C17 | 1.299(3) | | |
| Pb1-N4 | 2.4902(19) | N5-C17 | 1.305(3) | | |
| Pb1-03 | 2.701(2) | N4-N5 | 1.387(3) | | |
| O1-Pb1-N1 | 120.77(6) | O2-Pb1-N4 | 60.17(6) | N4-Pb1-O3 | 78.02(7) |
| 01-Pb1-N2 | 59.01(5) | O2-Pb1-O3 | 115.81(7) | N1-Pb1-O2' | 82.87(6) |
| 01-Pb1-N4 | 173.31(6) | N1-Pb1-N2 | 61.83(6) | N2-Pb1-O2' | 82.14(5) |
| O1-Pb1-O3 | 107.38(7) | N1-Pb1-N4 | 64.28(6) | N4-Pb1-O2' | 89.81(6) |
| O1-Pb1-O2 | 113.36(5) | N1-Pb1-O3 | 71.89(7) | 01-Pb1-02' | 86.65(7) |
| O2-Pb1-N1 | 119.54(5) | N2-Pb1-N4 | 126.08(6) | O2-Pb1-O2' | 75.15(6) |
| 02-Pb1-N2 | 156.63(5) | N2-Pb1-O3 | 87.24(8) | O3-Pb1-O2' | 154.71(7) |
| Hydrogen bonds (N−H, H··· | ·0, N···0, ∠NHO) | | | | |
| N3-H3A···05″ | 0.86 | 2.31 | 3.083(3) | 149.4 | |
| | | | | | |

Symmetry operators: (') -x, -y + 1, -z; (") -x + 1/2, y - 1/2, -z + 1/2.

Table 4

X-ray structure data collection and refinement parameters.

| | $[Pb(py)(L^{Ph})]$ | [Pb(HL ^{Ph})Cl] | [Pb(HL ^{Ph})Br] | [Pb(HL ^{Ph})I] | $[Pb(HL^{Ph})I] \cdot MeOH \cdot 0.5H_2O$ | $[Pb(HL^{Ph})(NO_3)]_2$ |
|--|--|--|--|---|---|-------------------------|
| Formula | C ₂₈ H ₂₄ N ₆ O ₂ Pb | C ₂₃ H ₂₀ ClN ₅ O ₂ Pb | C ₂₃ H ₂₀ BrN ₅ O ₂ Pb | C ₂₃ H ₂₀ IN ₅ O ₂ Pb | C ₂₄ H ₂₅ IN ₅ O _{3.5} Pb | C46H40N12O10Pb2 |
| M _w | 683.72 | 641.08 | 685.54 | 732.53 | 773.58 | 1335.28 |
| Crystal system | orthorhombic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| a (Å) | 20.8235(7) | 8.4151(17) | 8.4393(3) | 8.4644(2) | 15.8483(5) | 27.4709(8) |
| b (Å) | 11.4127(3) | 12.981(3) | 13.0932(5) | 13.2888(3) | 11.5216(4) | 8.5387(2) |
| <i>c</i> (Å) | 21.4438(6) | 20.321(4) | 20.4388(7) | 20.6322(5) | 16.2156(6) | 23.5924(7) |
| α (°) | 90 | 90 | 90 | 90 | 90 | 90 |
| β (°) | 90 | 94.50(3) | 92.979(2) | 90.7090(10) | 109.219(2) | 124.3640(10) |
| γ (°) | 90 | 90 | 90 | 90 | 90 | 90 |
| $V(Å^3)$ | 5096.2(3) | 2213.0(8) | 2255.38(14) | 2320.57(9) | 2795.91(17) | 4568.1(2) |
| Space group | Pbca | P21/c | $P2_1/c$ | P21/c | $P2_1/n$ | C2/c |
| Ζ | 8 | 4 | 4 | 4 | 4 | 4 |
| $D_{\text{calc.}}$ (g cm ⁻³) | 1.782 | 1.924 | 2.019 | 2.097 | 1.827 | 1.942 |
| μ (mm $^{-1}$) | 6.659 | 7.776 | 9.283 | 8.631 | 7.171 | 7.435 |
| No. of refl. | 59595 | 33935 | 39342 | 39 599 | 47684 | 67956 |
| No. of indep. | 7447 | 6845 | 6941 | 6982 | 8598 | 6884 |
| No. param. | 336 | 291 | 291 | 291 | 322 | 318 |
| R_1/wR_2 | 0.0222/0.0404 | 0.0425/0.0703 | 0.0333/0.0580 | 0.0260/0.0464 | 0.0508/0.1187 | 0.0205/0.0435 |
| Goodness-of-fit (GOF) on F^2 | 1.005 | 0.962 | 1.006 | 1.038 | 0.963 | 1.025 |

yellow solid, which can be assigned to a composition of $[Pb(H_2L^{Ph})(NO_3)_2]_2$ or $[Pb(H_2L^{Ph})(NO_3)_2]_n$ as has been discussed in an analogous manner before for the halido compounds. The IR spectrum of the precipitated material clearly confirms the coordination of the ligand without deprotonation. The v_{N-H} vibration is detected at 3228 cm⁻¹ and the $v_{C=0}$ frequency appears at 1648 cm⁻¹. The coordination of nitrate is supported by the bands at 1440 and 1383 cm⁻¹.

The solid readily dissolves in dimethylformamide or dimethyl sulfoxide forming yellow solutions. From both solvents, single crystals of the composition $[Pb(HL^{Ph})(NO_3)]_2$ could be obtained. Similar to the $[Pb(HL^{Ph})X]_2$ complexes (X = Cl, Br, I), dissolution in coordinating solvents results in monodeprotonation of the ligand, the elimination of HNO₃ and the final formation of a well-defined dimeric compound: $[Pb(HL^{Ph})(NO_3)]_2$.

 $[Pb(HL^{Ph})(NO_3)]_2$ crystallizes in the monoclinic space group C2/c. An ellipsoid representation of the asymmetric unit is shown in Fig. 4a. Table 3 contains selected bond lengths and angles. The Pb–O bonds inside the five-membered chelate rings of the pentadentate ligand are 2.751(2) (Pb1–O1) and 2.708(2) Å (Pb1–O2). This means, they are almost equal, which is in contrast to the halide complexes, which also possess monodeprotonated $[L^{Ph}]^-$ ligands. Surprisingly short Pb–O bonds of 2.442(2) Å, however, are established between the lead(II) ions and the O2' donors of the adjacent chelate (symmetry code: -x, -y + 1, -z). They establish the coordination dimers of $[Pb(HL^{Ph})(NO_3)]_2$ as is illustrated in

Fig. 3b. The nitrate ion is coordinated to the Pb atom through the O3 atom with a distance of 2.701(2) Å, which is longer than the Pb–O bond lengths found in other Pb/monohydrazone complexes with coordinated nitrate [13,29]. As in the other two crystal structures with nitrato ligands [13,29], a second oxygen atom (O5 atom) of the nitrate weakly interacts with Pb. In [Pb(HL^{Ph})(NO₃)]₂, this contact is relatively long (3.309(2) Å), since this oxygen atom establishes an intermolecular hydrogen bond to the nitrogen atom of the "non-deprotonated arm" of an adjacent complex molecule. These N–H···O hydrogen bonds arrange the dimeric complex molecules to a two-dimensional network in the (10–1) plane as is shown in Fig. 4c.

3. Conclusions

The coordination chemistry of 2,6-diacetylpyridine-*bis*(benzoylhydrazone) with lead(II) goes beyond the simple formation of complexes with pentadentate organic ligands. The use of different Pb(II) salts in essentially similar reactions results in supramolecular assemblies of different arrangements depending on the starting materials and the reaction conditions. Weak intermolecular Pb···N interactions, π -stacking or hydrogen bonds organize the products in different dimeric arrangements ([Pb(py) (L^{Ph})]₂, [Pb(HL^{Ph})Cl]₂, [Pb(HL^{Ph})Br]₂) or supramolecular assemblies with dimeric sub-structures ([Pb(HL^{Ph})I]₂, [Pb(HL^{Ph})(NO₃)]₂).

4. Experimental

4.1. Materials

All reagents used were reagent grade and used without further purification. H_2L^{Ph} was prepared from equivalent amounts of 2,6-diacetylpyridine and benzoylhydrazine in ethanol following literature procedures [30,31].

4.2. Physical measurements

Infrared spectra were measured from KBr pellets on a Bruker Tensor 27 FTIR instrument between 400 and 4000 cm⁻¹. Elemental analysis of carbon, hydrogen and nitrogen were determined using a Perkin Elmer CHN 2400 elemental analyzer. NMR-spectra were taken with a Bruker DPX-NMR 400 MHz multinuclear spectrometer.

4.3. Syntheses

4.3.1. $[Pb(L^{Ph})]_n$

A solution of Pb(OAc)₂·3H₂O (100 mg, 0.26 mmol) in 4 mL of MeOH was added dropwise to a suspension of H_2L^{Ph} (105 mg, 0.26 mmol) in 8 mL of MeOH. After the complete addition of the ligand, 10 drops of Et₃N were added and the reaction mixture was stirred for additional 2 h. The formed solid was filtered off and washed with MeOH. Yield: 99%. *Anal.* Calc. for C₂₃H₁₉N₅O₂Pb: C, 45.69; H, 3.17; N, 11.58. Found: C, 45.54; H, 3.06; N, 11.35%. IR (KBr, v_{max} in cm⁻¹): 3060 (w), 2909 (w), 1583 (w), 1538 (w), 1497 (m), 1474 (w), 1406 (w), 1350 (s), 1320 (m), 1295 (m), 1175 (m), 1159 (m), 1049 (w), 1001 (w), 898 (w), 798 (w), 732 (w), 707 (m), 685 (w), 672 (w), 500 (w).

4.3.2. $[Pb(py)(L^{Ph})]_2$

The solid of $[Pb(L^{Ph})]_n$ (50 mg) was dissolved under stirring in 10 mL of neat pyridine, which resulted in an yellow solution. This solution was mixed with 5 mL MeOH and kept for slow evaporation at room temperature, which gave yellow, block-shaped single crystals of $[Pb(py)(L^{Ph})]_2$. Yield: 90%. *Anal.* Calc. for $C_{28}H_{24}N_6O_2Pb$: C, 49.19; H, 3.54; N, 12.29. Found: C, 49.17; H, 3.93; N, 12.10%. IR (KBr, v_{max} in cm⁻¹): 3046 (w), 2920 (w), 1583 (w), 1536 (m), 1508 (m), 1479 (m), 1450 (m), 1405 (w), 1348 (s), 1312 (m), 1291 (m), 1216 (w), 1168 (m), 1150 (m), 1064 (w), 1031 (m), 1001 (m), 976 (w), 911 (w), 847 (w), 798 (m), 767 (m), 732 (w), 714 (s), 670 (m), 621 (m), 510 (w), 415 (w).

4.3.3. $[Pb(H_2L^{Ph})X_2]_n (X = Cl, Br, I)$

A suspension of H_2L^{Ph} (48 mg, 0.12 mmol) in 4 mL of MeOH was added dropwise to suspensions of PbX₂ (0.1 mmol) in 2 mL of MeOH. After the complete addition of the ligand, the yellow to orange turbid reaction mixtures were stirred at room temperature for 2 h. The resulting solids were filtered off and washed with MeOH.

4.3.3.1. $[Pb(H_2L^{Ph})Cl_2]_n$. Yield: 86%. Anal. Calc. for $C_{23}H_{21}Cl_2N_5O_2Pb$: C, 40.77; H, 3.12; N, 10.34. Found: C, 40.58; H, 3.16; N, 9.98%. IR (KBr, v_{max} in cm⁻¹): 3143 (w), 2940 (w), 1641 (s), 1616 (m), 1600 (m), 1577 (m), 1531 (s), 1489 (m), 1452 (m), 1432 (m), 1372 (m), 1274 (s), 1156 (m), 1117 (w), 1074 (w), 1010 (w), 896 (w), 805 (m), 736 (m), 713 (s), 688 (m), 529 (w), 457 (w).

4.3.3.2. $[Pb(H_2L^{Ph})Br_2]_n$. Yield: 76%. Anal. Calc. for $C_{23}H_{21}Br_2N_5O_2Pb$: C, 36.04; H, 2.76; N, 9.14. Found: C, 35.72; H, 2.85; N, 8.76%. IR (KBr, v_{max} in cm⁻¹): 3351 (w), 3027 (w), 1654 (s), 1616 (m), 1598 (m), 1578 (m), 1523 (m), 1483 (m), 1449 (m), 1427 (m), 1379 (w), 1290 (w), 1264 (s), 1164 (m), 1155 (m), 1118 (w), 1071 (w), 999 (w), 897 (w), 801 (m), 709 (s), 683 (w), 658 (w), 478 (w).

4.3.3.3. $[Pb(H_2L^{Ph})I_2]_n$. Yield: 92%. Anal. Calc. for $C_{23}H_{21}I_2N_5O_2Pb$: C, 32.10; H, 2.46; N, 8.14. Found: C, 31.71; H, 2.49; N, 7.69%. IR (KBr, v_{max} in cm⁻¹): 3367 (w), 3024 (w), 1657 (s), 1614 (m), 1597 (m), 1577 (m), 1517 (m), 1480 (m), 1447 (m), 1376 (w), 1290 (w), 1261 (s), 1165 (m), 1155 (m), 1118 (w), 1069 (w), 999 (w), 898 (w), 799 (m), 707 (m), 682 (w), 657 (w), 467 (w).

4.3.4. $[Pb(HL^{Ph})X]_2$ (X = Cl, Br, I)

Recrystallization of the $[Pb(H_2L^{Ph})X_2]_2$ (X = Cl, Br, I) complexes from neat DMSO or DMSO/MeOH mixtures resulted in HX abstraction and the formation of yellow, block-shaped single crystals of the $[Pb(HL^{Ph})X]_2$ complexes.

4.3.4.1. [*Pb*(*HL*^{*Ph*})*Cl*]₂. Yellow crystals. Yield: 60%. *Anal.* Calc. for C₂₃-H₂₀ClN₅O₂Pb: C, 43.09; H, 3.14; N, 10.92. Found: C, 41.65; H, 3.25; N, 10.09%. IR (KBr, v_{max} in cm⁻¹): 3242 (w), 3050 (w), 1667 (s), 1581 (w), 1533 (w), 1505 (s), 1449 (w), 1417 (w), 1347 (s), 1315 (w), 1300 (w), 1265 (m), 1196 (w), 1175 9w), 1147 (m), 1067 (w), 1034 (m), 1022 (m), 936 (w), 895 (w), 804 (m), 735 (w), 711 (s), 689 (m), 677 (m), 664 (m), 500 (w). ¹H NMR (DMSO-*D*₆; δ , ppm): 2.52 (s, 6H, CH₃), 7.51–7.62 (m, 6H, Ph), 7.91–7.93 (m, 5H, py + Ph), 8.06 (br, 2H, py), 10.87 (s, 1H, NH).

4.3.4.2. [*Pb*(*HL*^{*Ph*})*Br*]₂. Yellow crystals. Yield: 75%. *Anal.* Calc. for C₂₃-H₂₀BrN₅O₂Pb: C, 40.30; H, 2.94; N, 10.22. Found: C, 40.08; H, 3.01; N, 9.99%. IR (KBr, v_{max} in cm⁻¹): 3262 (w), 3050 (w), 1670 (s), 1581 (w), 1522 (w), 1507 (s), 1449 (w), 1417 (w), 1347 (s), 1316 (w), 1300 (w), 1265 (m), 1197 (w), 1175 (w), 1147 (m), 1067 (w), 1033 (m), 1022 (m), 937 (w), 895 (w), 804 (m), 734 (w), 712 (s), 689 (m), 677 (m), 664 (m), 499 (w). ¹H NMR (DMSO-*D*₆; δ , ppm): 2.58 (s, 6H, CH₃), 7.52–7.63 (m, 6H, Ph), 7.94–7.96 (m, 4H, Ph), 8.03 (br, 1H, py), 8.11 (br, 2H, py), 11.05 (s, 1H, NH).

4.3.4.3. [*Pb*(*HL*^{*Ph*})*I*]₂. Yellow crystals. Yield: 70%. *Anal.* Calc. for C₂₃-H₂₀IN₅O₂Pb: C, 37.71; H, 2.75; N, 9.56. Found: C, 37.77; H, 2.83; N, 9.32%. IR (KBr, v_{max} in cm⁻¹): 3265 (w), 3048 (w), 1673 (s), 1581 (w) 1550 (w), 1508 (s), 1450 (w), 1417 (w), 1347 (s), 1316 (w), 1299 (w), 1265 (m), 1199 (w), 1174 (w), 1148 (m), 1067 (w), 1033 (m), 999 (w), 936 (w), 896 (w), 804 (m), 791 (w), 733 (w), 714 (s), 689 (m), 678 (m), 664 (m), 497 (w). ¹H NMR (DMSO-*D*₆; δ , ppm): 2.65 (s, 6H, CH₃), 7.55–7.67 (m, 6H, Ph), 7.99–8.01 (m, 4H, Ph), 8.21 (br, 3H, py), 11.47 (s, 1H, NH).

Yellow crystals of $[Pb(HL^{Ph})I]_2 \cdot 2MeOH \cdot H_2O$ were obtained as a mixture when a small amount of the solution was let over a glass plate during the night.

4.3.5. $[Pb(H_2L^{Ph})(NO_3)_2]_2$ and $[Pb(HL^{Ph})(NO_3)]_2$

4.3.5.1. $[Pb(H_2L^{Ph})(NO_3)_2]_2$. A suspension of H_2L^{Ph} (48 mg, 0.12 mmol) in 4 mL of MeOH was added dropwise to a suspension of Pb(NO₃)₂ (33 mg, 0.1 mmol) in 2 mL of MeOH. The resulting yellow turbid solution was stirred at room temperature for 2 h. The pale yellow solid was filtered off and washed with MeOH. Yield: 85%. *Anal.* Calc. for C₂₃H₂₁N₇O₈Pb: C, 37.81; H, 2.90; N, 13.42. Found: C, 37.85; H, 2.93; N, 13.15%. IR (KBr, v_{max} in cm⁻¹): 3228 (w), 3047 (w), 1684 (s), 1618 (w), 1601 (w), 1579 (m), 1536 (m), 1491 (w), 1440 (m), 1383 (m), 1273 (s), 1166 (m), 1074 (w), 1027 (w), 898 (w), 805 (w), 735 (w), 711 (m), 686 (w), 663 (w), 529 (w).

4.3.5.2. $[Pb(HL^{Ph})(NO_3)]_2$. Light-yellow, block-shaped crystals were obtained by recrystallization from deutered DMSO or DMSO/MeOH mixture. Yield: 52%. *Anal.* Calc. for C₄₆H₄₀N₁₂O₁₀Pb₂: C, 41.38; H,

3.02; N, 12.59. Found: C, 41.52; H, 3.35; N, 12.38%. IR (KBr, ν_{max} in cm⁻¹): 3214 (w), 3083 (w), 1658 (s), 1581 (w), 1530 (m), 1487 (m), 1385 (s), 1346 (s), 1310 (s), 1199 (w), 1148 (m), 1067 (w), 1035 (m), 933 (w), 897 (w), 806 (m), 717 (m), 693 (w), 677 (w), 533 (w). ¹H NMR (DMSO- D_6 ; δ , ppm): 2.65 (s, 6H, CH₃), 7.55–7.67 (m, 6H, Ph), 8.00–8.02 (m, 4H, Ph), 8.21 (br, 3H, py), 11.74 (s, 1H, NH).

4.4. X-ray crystallography

The intensities for the X-ray determinations were collected on a Bruker CCD X8 Kappa APEX II diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS and SHELXL [32]. Hydrogen atom positions were calculated for idealized positions and treated with the 'riding model' option of SHELXL. All crystals of [Pb(HL^{Ph})Cl]₂ were twinned (in a non-merohedral twinning type). Thus, the reflections of each component were adequately separated with APEX II for data reduction. The overlapping reflections were included for the refinement to obtain the completeness of the data. At the end, the structure could be correctly refined. More details on data collections and structure calculations are contained in Table 4. Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre.

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Appendix A. Supplementary data

CCDC 1448755, 1448756, 1448757, 1448758, 1448759 and 1448760 contains the supplementary crystallographic data for [Pb(py)(L^{Ph})]₂, [Pb(HL^{Ph})Cl]₂, [Pb(HL^{Ph})Br]₂, [Pb(HL^{Ph})I]₂, [Pb(HL^{Ph}) I]₂·2MeOH·H₂O and [Pb(HL^{Ph})(NO₃)]₂, respectively. 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.

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