

Heptacoordinated diphenyllead; hexa- and pentacoordinated triphenyllead and tin compounds derived from 5H-benzimidazo[1,2-c]quinazoline-6-thione

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ABSTRACT

Heptacoordinated diphenyllead; hexa- and pentacoordinated triphenyllead and tin compounds derived from 5H-benzimidazo[1,2-c]quinazoline-6-thione are reported. The same molecular structures were found in solution by ^{119}Sn and ^{207}Pb NMR and in the solid state by X-ray diffraction analysis. The ligand was bound through S and N giving a four-membered ring. Due to the tension of the chelate ring in the penta- and hexacoordinated compounds, the nitrogen approaches the metal atom from an oblique direction giving a weak coordination. Hexacoordinated metal atoms were obtained by Lewis bases coordination to the polycyclic tin and lead compounds, which was possible because the *M*-phenyl groups form a cavity that allows the bases to approach from the opposite direction to the sulfur atom. In some crystals, two molecules formed a cavity where a solvent molecule was included. A heptacoordinated diphenyllead bound to two ligands and having the less common pentagonal bipyramidal geometry and *cis-mer* configuration with two sulfur atoms lying very close together was obtained.

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1. Introduction

We are interested in the study of planar polycyclic aromatic compounds bearing nitrogen and sulfur atoms which could have relevance as cytotoxic or antitumor agents through DNA intercalation. Derivatives of 5H-benzimidazo[1,2-c]quinazoline-6-thione (**1**) are interesting due to their cytotoxic [1], antihelmintic [2], virucides and neoplasm inhibitors [3] or antibacterial activities [4]. In addition, heterocyclic compounds having the C=S group have bio-cidal and antitumoral activities and application in analytical chemistry and medicine [5–7].

The lone pairs and labile protons of the nitrogen aromatic heterocycles make them suitable ligands for metal atoms. In this context, we have especially focused our studies on their coordination to metal atoms with environmental and toxicological relevance, such as tin and lead, which give a rich variety of coordination numbers and geometries [8–11]. Lead derivatives are especially interesting because they give more stable compounds with higher coordination numbers and are the less explored.

In spite of numerous and diverse syntheses of **1** [1,2,4,12–18], and that it is a starting material for biologically active compounds and pharmaceuticals [12,13], neither its X-ray diffraction structure nor its ^{13}C NMR spectrum have been reported. This information is important in order to establish its preferred tautomer and possible

metallic coordination modes. It has been proposed that compound **1** is a thiol [1,17].

2. Results and discussion

2.1. General comments

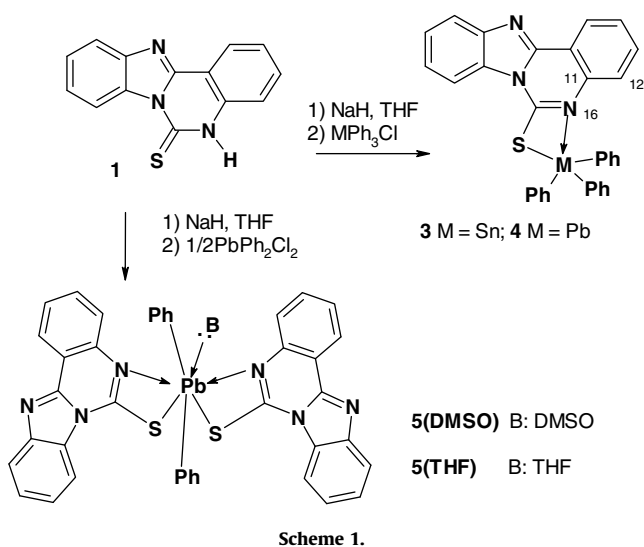
Herein, we report the syntheses of phenyl tin and phenyl lead organometallic compounds derived from 5H-benzimidazo[1,2-c]quinazoline-6-thione (**1**). Reactions were performed using the sodium amide (**2**) of **1** and MPh_3Cl ($\text{M}=\text{Sn}$ and Pb) or PbPh_2Cl_2 in THF, Scheme 1.

Structures of the starting heterocycle and the coordination compounds were analyzed in solution by ^1H , ^{13}C , ^{15}N , ^{119}Sn and ^{207}Pb NMR. Unequivocal assignments were performed by 2D experiments [COSY, HETCOR and COLOC]. Crystalline structures were studied by X-ray diffraction.

The aromatic tetracycle **1** has, as possible reactive sites, a basic sp^2 nitrogen atom, a thione or a thiol group and a labile N–H proton that could be located at N1, N16 or at the sulfur atom, giving three possible tautomers. Therefore, not only the preferred tautomer of **1**, but the structure of the tin and lead compounds depends on the competition between the different reactive sites, Scheme 2.

The ^{13}C NMR spectrum of **1** in DMSO (+28 °C) showed the characteristic thione signal at 169.2 ppm, whereas its ^{15}N spectrum in DMSO- d_6 (+80 °C) presented three signals assigned by comparison with reported indolizine compounds [19]: two singlets, at –195.6 ppm (N3) and –146.3 ppm (N1) and a doublet at

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–225.6 ppm for N16–H [$\{^1J(^{15}N-H)\} = 93.6$ Hz], which clearly shows that the preferred tautomer in solution has the labile proton at N16.

The solid state structure of **1** was obtained by X-ray diffraction analyses, one polymorph was crystallized from $CHCl_3$ (**1a**) and a second (**1b**) from acetone or EtOH. Both crystalline structures have a proton at N16, Fig. 1. It has two intramolecular hydrogen bonds, one between H4 and sulfur, and the other between N1 and H15, Fig. 1.

The polymorph **1a** (monoclinic, $C2/c$) forms a polymer organized in planar ribbons by the presence of cooperative hydrogen bonds, Fig. 2. The second polymorph **1b** (monoclinic, $P2_1/n$) presents two intermolecular hydrogen bonds and π stacking, Fig. 3.

The sodium amide (**2**) was obtained by reaction of compound **1** with NaH in THF and directly analyzed by NMR. The 1H NMR spectrum did not show the NH proton signal. The electron withdrawing effect of the N16-lone pair shifted the ^{13}C resonances to higher

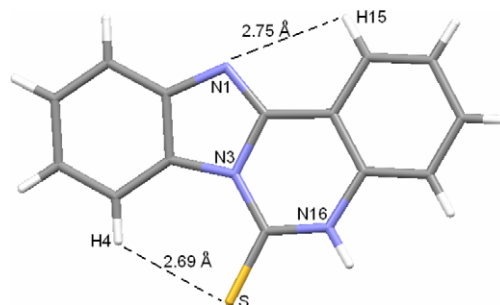
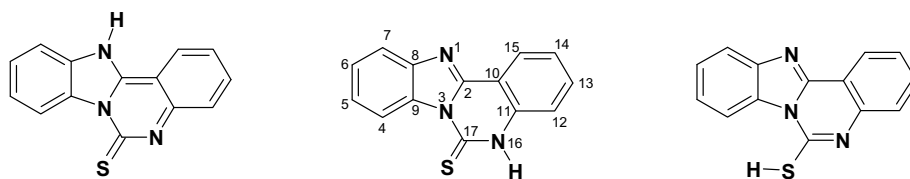


Fig. 1. X-ray diffraction structure of compound **1** showing the preferred tautomer and intramolecular hydrogen bonds.

frequencies C2 ($\Delta\delta = 3.2$ ppm), C10 ($\Delta\delta = 2.1$ ppm), C11 ($\Delta\delta = 8.4$ ppm) and C12 ($\Delta\delta = 8.6$ ppm) which confirmed that N16 was protonated in compound **1**. The ^{15}N spectrum indicated that the N16 signal was shifted from $\delta = -225.2$ ppm in **1** to -158.9 ppm in **2**. The other two signals remained constant (N1 $\delta = -142.7$ ppm, N3 $\delta = -191.1$ ppm). Compound **2** was reacted *in situ* with $SnPh_3Cl$, $PbPh_3Cl$ and Pb_2PbCl_2 .

2.2. Tin compounds

The reaction of **2** with $SnPh_3Cl$ in THF afforded a light brown crystalline powder (**3**), Scheme 1. The ^{13}C NMR spectra ($CDCl_3$ or $DMSO-d_6$) showed the C–S single bond character (152.5 ppm) and the shift of C11 and C12 to higher frequencies showed the presence of a lone pair at the N16. The ^{119}Sn resonance in $CDCl_3$ or THF appeared at -114.7 ppm, shifted by 50 ppm to lower frequencies when compared with the value for a thiophenolate tin compound [$SnPh_3SPh$ ($CDCl_3$) appears at -64.3 ppm, Table 1]. The tin signal of **3** is similar to that of a 2-thiopyridine triphenyltin derivative ($\delta = -116.3$ ppm) [20], therefore, it was concluded that tin was bonded to the sulfur and coordinated by N16. The nitrogen and sulfur chelate forms a four-membered ring, giving a pentacyclic fused system bearing a pentacoordinated tin atom. This type of chelate has been reported for tin and lead compounds [20–25].



Scheme 2. Tautomers of compound **1**.

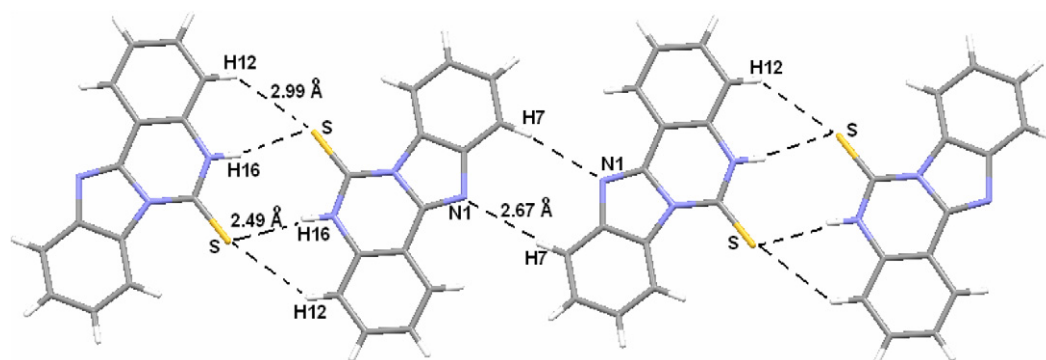


Fig. 2. H-bonds, $N \cdots H-C$, $C=S \cdots H-N$ and $C=S \cdots H-C$, in the cell of polymorph **1a** crystallized from $CHCl_3$.

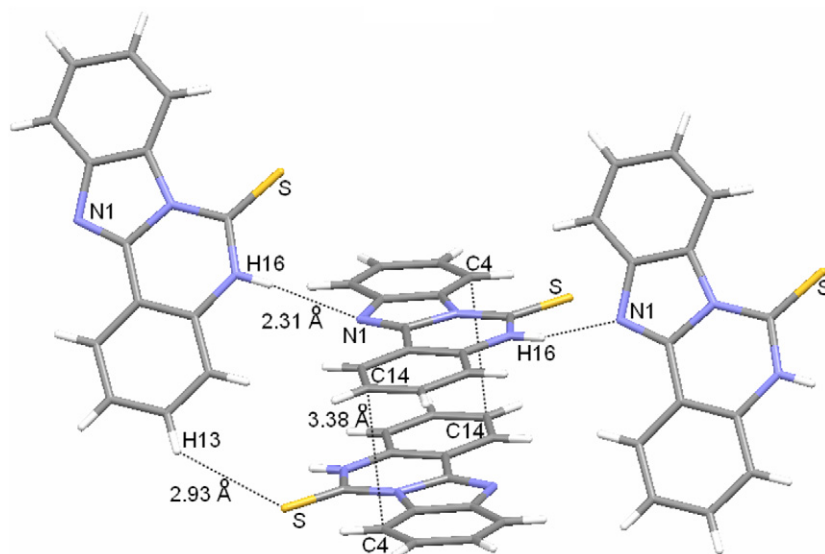


Fig. 3. Interactions in the net of the polymorph **1b** obtained from acetone.

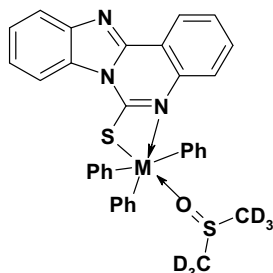
Table 1
 ^{119}Sn or ^{207}Pb and ^{13}C NMR data of **3–5** and other related compounds

Tin compounds – solvent	δ ^{119}Sn	M–Ct $^1J(^{119}/^{117}\text{Sn}, ^{13}\text{C})$
SnPh ₃ SPh – CDCl ₃	–64.3	137.6 (561, 536)
SnPh ₃ SPh – THF- <i>d</i> ₈	–66.5	137.8 (571, 531)
SnPh ₃ SPh – DMSO- <i>d</i> ₆	–140.1	142.2 (568, 541)
3 – THF	–114.7	140.0 (606, 579)
3 – CDCl ₃	–114.7	140.0 (599, 576)
3 – DMSO- <i>d</i> ₆	–231.7	143.7 (766, 732)
Lead compounds – solvent	δ ^{207}Pb	M–Ct $^1J(^{207}\text{Pb}, ^{13}\text{C})$
PbPh ₃ SPh – CDCl ₃	–14	153.1 (491.1)
PbPh ₃ SPh – THF- <i>d</i> ₈	–24	153.4 (508.1)
PbPh ₃ SPh – DMSO- <i>d</i> ₆	–100	156.1 (not obs.)
4 – CDCl ₃	–68	156.5 (553.5)
4 – DMSO- <i>d</i> ₆	–227	160.3 (754.7)
5 – DMSO- <i>d</i> ₆	–523	173.4 (1729.3)

The ^{119}Sn spectrum of compound **3** dissolved in DMSO-*d*₆ showed a signal at –231.7 ppm, characteristic of a hexacoordinate tin atom, as a result of DMSO coordination [26].

Crystallization of compound **3** from THF/DMSO (10:1) gave crystals (**3a**) without solvent in the lattice, Fig. 4. Crystallization from CDCl₃ (**3b**), THF (**3c**), acetone (**3d**) and DMSO (**3e**) gave isomorphous crystals (triclinic *P* $\bar{1}$) which contain a solvent molecule in the cavity formed by the cones of two SnPh₃ groups, Fig. 5.

Crystals **3b–3e** contain solvent (disordered) which can appear in either of two orientations. The distances of the solvent molecules to the tin atoms are longer than the sum of the van der Waals



Scheme 3. Hexacoordinated compounds (M=Sn) and (M=Pb).

radii [27], with the exception of the structure having DMSO (**3e**), Fig. 5. In crystals **3e**, the oxygen atom of the DMSO is pointing to the tin within a distance of 3.05(2) Å. Sulfur and oxygen atoms are in *trans* position, forming a S–Sn–O angle of 174.6°. Compound **3** in the different crystals **3a–3e** with or without solvent has the same structure with similar angles and bond lengths, Table 2.

The tin geometry in crystals **3a–3e** is a distorted *tbp*, the apical positions are occupied by a phenyl group and the nitrogen atom [N16–Sn–C32 are in the range of 152.3(2)–159.4(2)°]. The distance N → Sn (from 2.82 to 2.88 Å) is shorter than the sum of the van der Waals radii ($\Sigma r_{\text{cov}} \text{Sn–N} = 2.15 \text{ Å}$; $\Sigma r_{\text{vdW}} \text{Sn–N} = 3.85 \text{ Å}$) [27]. Other reported tin compounds bound to thiourea aromatic molecules form S,N four-membered ring chelates, their bond lengths Sn–S appear between 2.44 and 2.53 Å and N → Sn bonds between 2.43 and 3.16 Å [20,21,24,25]. Crystals **3a–3e** are stabilized by C–H···N, C–H··· π hydrogen bonds and π interactions, Figs. 6 and 7.

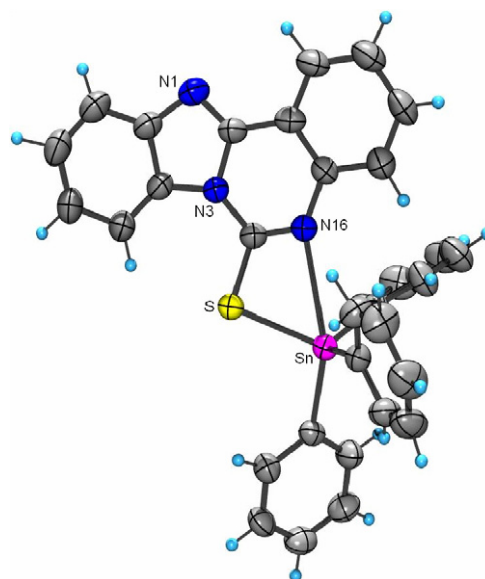


Fig. 4. ORTEP diagram of compound **3a**.

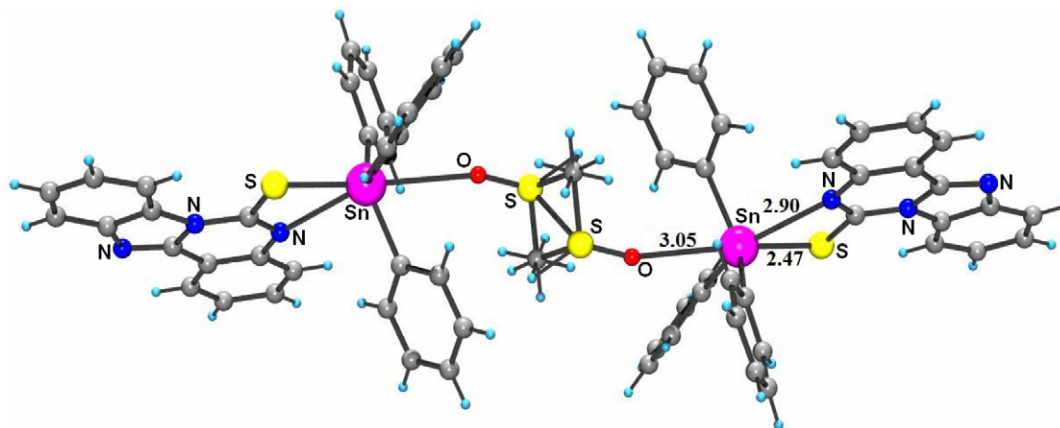
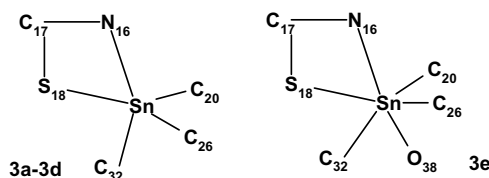


Fig. 5. X-ray diffraction of crystalline structure of isomorph 3e.

Table 2

Bond lengths (Å) and angles (°) of compound 3 in crystals 3a–3e



Átoms	3a	3b	3c	3d	3e
N16–Sn	2.819(4)	2.883(3)	2.881(3)	2.872(3)	2.901(4)
S18–Sn	2.479(2)	2.460(1)	2.465(1)	2.463(1)	2.473(2)
C17–S18	1.742(5)	1.743(4)	1.746(4)	1.746(4)	1.747(5)
C17–N16	1.290(6)	1.302(4)	1.293(4)	1.294(5)	1.289(7)
Sn...Cl or O38	–	4.402(4)	3.81(3)	4.46(1)	3.05(2)
N16–Sn–C32	159.4(2)	153.7(1)	153.7(1)	153.6(1)	152.3(2)
S18–Sn–C20	110.9(1)	110.6(1)	112.5(1)	113.4(1)	109.6(2)
S18–Sn–C26	114.2(2)	113.1(1)	110.6(1)	111.0(1)	111.2(1)
S18–Sn–C32	100.9(2)	95.50(1)	95.8(1)	95.5(1)	94.7(2)
C20–Sn–C26	116.5(2)	120.5(2)	120.8(2)	119.8(2)	122.3(2)
C26–Sn–C32	107.2(2)	106.9(1)	106.7(1)	107.1(2)	107.8(2)
C32–Sn–C20	105.5(2)	107.1(1)	107.1(1)	106.8(1)	107.6(2)

2.3. Lead compounds

Lead(IV) compounds were prepared from PbPh_3Cl and PbPh_2Cl_2 and 1 or 2 equiv. of the sodium amide 2 in THF. The reaction products were analyzed by ^{207}Pb NMR. The reaction between amide 2 and PbPh_3Cl in equimolar ratio afforded mainly compound 4, and 2% of a compound identified as 5. ^{13}C and ^1H NMR analyses of 4 confirmed that it has a similar structure to tin compound 3, with the lead chelated by sulfur and nitrogen atoms, Scheme 1.

Comparison of ^{207}Pb data and coupling constants $^1J(^{207}\text{Pb}-^{13}\text{C})$ of compound 4 with Ph_3PbSPh in different solvents allows evaluation of the $\text{N} \rightarrow \text{Pb}$ coordination bond in compound 4, Table 1. The strong effect of the $\text{DMSO}-d_6$ on the chemical shift of compound 4 ($\delta = -227.0$ ppm) shows that the solvent coordination afforded the hexacoordinated lead compound 4a, Scheme 3.

The reaction of 2 equiv. of ligand 2 and PbPh_2Cl_2 gave compound 5, Scheme 1. The ^{207}Pb chemical shift of compound 5(DMSO) ($\delta = -523$ ppm) in DMSO corresponds to a highly coordinated compound, bound by two ligands and DMSO. The heptacoordinated structure was confirmed later by X-ray diffraction analysis of the corresponding THF complex 5(THF).

From the reaction product containing the mixture of 4 and 5, crystals of each compound were obtained and their structures determined by X-ray diffraction. Compound 4, co-crystallized with a CHCl_3 molecule (triclinic $P\bar{1}$), has a similar structure to 3b. It is a

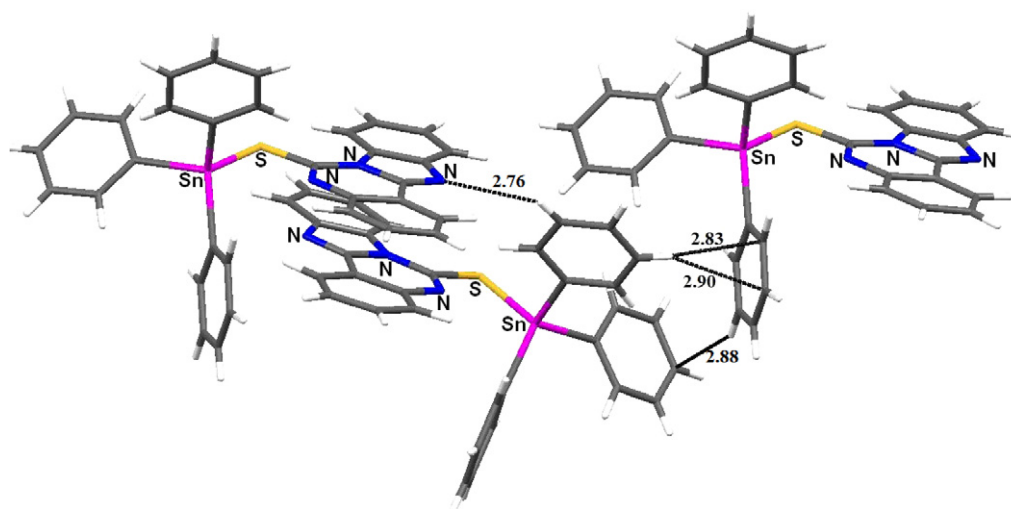


Fig. 6. C–H...N, C–H... π H-bonds in 3a.

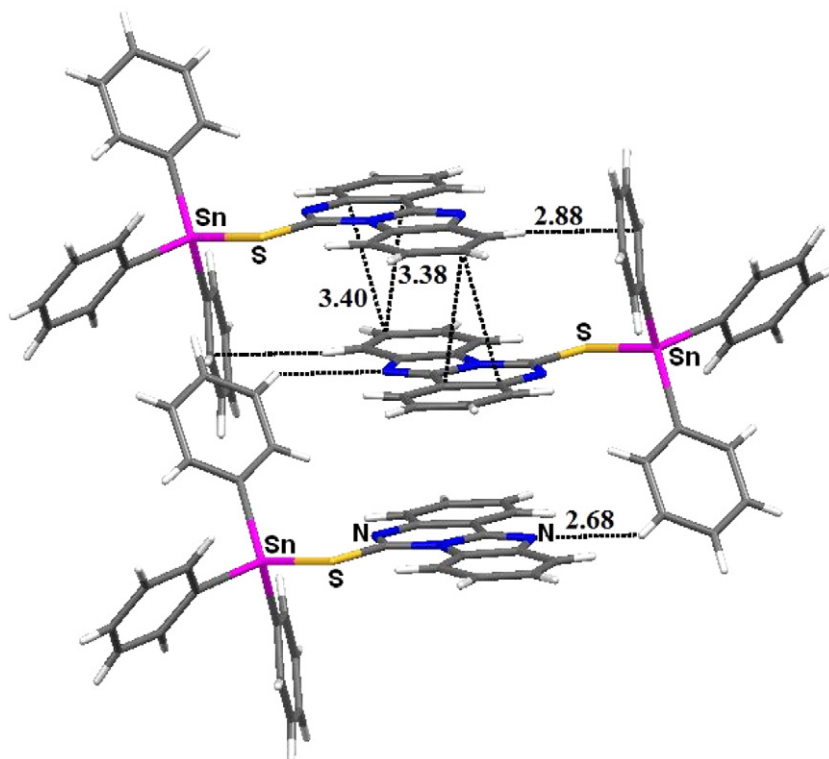


Fig. 7. π -Interactions and H-bonds in **3b**.

pentacoordinated triphenyllead compound with a covalent bond to sulfur and coordination to the nitrogen atom. Two molecules form a cavity, where a solvent molecule is found. The lead molecule **4** forms dimers by π -stacking, Fig. 8.

Compound **5**, has a heptacoordinated lead atom, bound to two ligands (*cis-mer* isomer) and two phenyl groups. One molecule of THF was also coordinated to the lead atom (Pb–O26 3.26 Å; Σr_{vdW} = 3.52 Å), Fig. 9.

The lead atom is a distorted pentagonal bipyramid with the phenyl groups occupying the apical positions and a pentagonal plane depicted by two sulfurs, two nitrogens and the oxygen of the THF, Fig. 10. The two ligands are arranged in the equatorial plane. Selected bond lengths and angles are in Table 3. To our knowledge, compound **5** is the second example of a heptacoordinated diphenyllead atom having an O \rightarrow Pb coordination bond, the first being reported by Casas et al. [23].

The S–Pb bonds [2.65 Å (Σr_{vdW} = 3.80 Å)] are shorter than N16–Pb bonds [2.77 Å (Σr_{vdW} = 3.55 Å)]. There is an interesting distortion of the geometry around the lead atom. The sulfur atoms are in *cis* position, with a short interligand S...S contact of 3.40 Å, (Σr_{vdW} S–S = 3.60 Å), the angle S–Pb–S is very closed (79.74°) whereas the N–Pb–N is very open (165.47°). The C–Pb–C bonds have an angle of 145.8° instead of the expected value of 180°. There is no steric reason for the small S–Pb–S angle and the short S...S distance as there is enough room for the two chelates which would allow the sulfur atoms to separate themselves, according to VSEPR theory [28]. A coordinated THF occupies the cavity formed between the two phenyl and two phenylene groups, although this does not appear to be the reason for the open N–Pb–N angle. There are examples of other diphenyltin and diphenyllead compounds having two S N four-membered chelates rings, which have the same distortion with closed S–

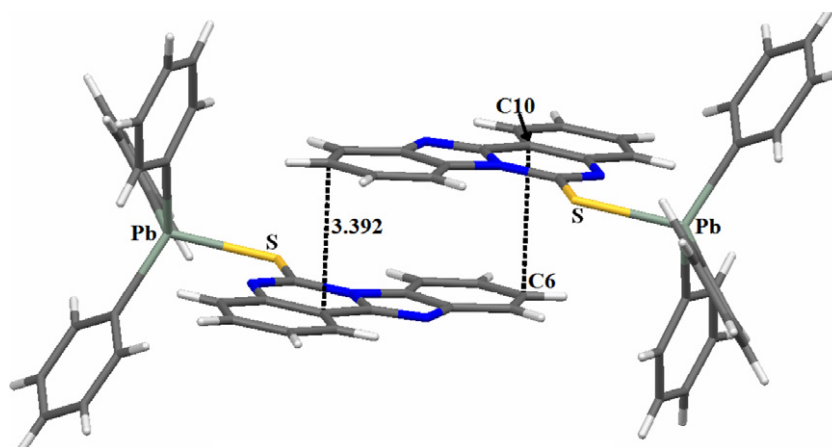


Fig. 8. π -Stacking in compound **4**.

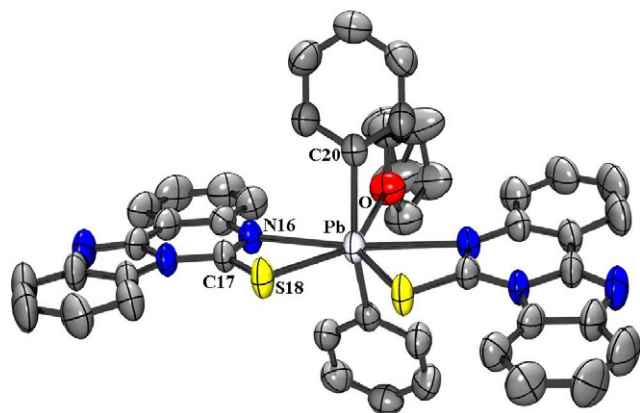


Fig. 9. Solid state structure of compound 5(THF).

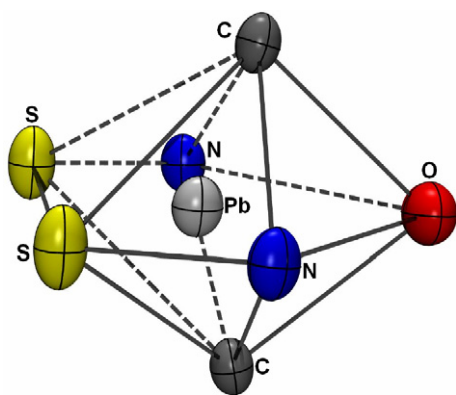


Fig. 10. Coordination sphere around the lead atom in 5.

Pb–S and C–Pb–C angles and an open N–Pb–N angle [29–32]. An example is shown in Fig. 11 [22].

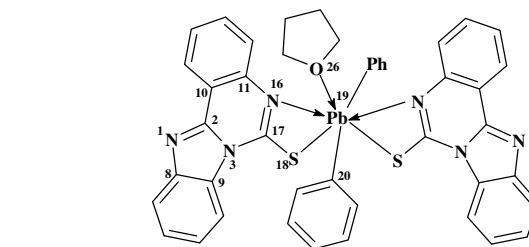
The distortion of compound 5 could be the result of a stabilizing interaction between the sulfur atoms $S \cdots S$, as it has been pointed out for molybdenum compounds such as in Fig. 12 [33], or the effect of π -donor ligands competing for a given set of metal d-orbitals [28].

The THF coordination in compound 5(THF) merits some comments. In addition to the $O \rightarrow Pb$ coordination, the THF was also bound by two hydrogen bonds between the *ortho* CH protons of the phenylene groups and the oxygen atom, which becomes pentacoordinated ($O26 \cdots H12$, 2.55 Å, $O26-H12-C12 = 173.2^\circ$), Fig. 13. Each nitrogen atom forms two hydrogen bonds with the *ortho* C–H of the Pb–phenyl groups producing a pentacoordinated nitrogen atom $N16 \cdots H25$ (2.46 Å, $N16-H25-C25 = 135.6^\circ$), $N16 \cdots H21$ (2.47 Å, $N16-H21-C21 = 140.1^\circ$). Sulfur atoms also present intramolecular H-bonds $S18 \cdots H4$ (2.64 Å, $S18-H4-C4 = 122.7^\circ$), Fig. 14.

3. Summary

The preferred tautomer of the ligand 5H-benzimidazo[1,2-*c*]quinazoline-6-thione 1 and the corresponding phenyl lead and tin organometallic derivatives were fully characterized in solid state and in solution. ^{119}Sn and ^{207}Pb NMR gave enough information to determine the coordination number of the metal atoms and the ligand coordination mode in solution. The ligand was bound through S and N forming four-membered rings. Due to the tension of the chelate ring, the nitrogen approaches the metal atom from an oblique direction giving, by a weak coordination, the penta- or hexacoordination of the metal atom. The polycyclic tin and

Table 3
Bond lengths (Å) and angles ($^\circ$) for compound 5(THF)



N1–C2	1.304(5)	N16–C17	1.295(5)
N1–C8	1.388(7)	N16–Pb	2.765(3)
C2–N3	1.402(5)	C17–S18	1.718(4)
C2–C10	1.433(7)	S18–Pb	2.6500(9)
N3–C9	1.408(5)	Pb–C20	2.191(4)
N3–C17	1.392(4)	Pb–O32	3.258(5)
C11–N16	1.391(5)		
C2–N1–C8	105.2(4)	C10–C11–N16	121.7(4)
N1–C2–N3	112.6(4)	C12–C11–N16	118.7(4)
N1–C2–C10	129.9(4)	C11–N16–C17	120.8(3)
N3–C2–C10	117.5(3)	C11–N16–Pb	145.0(2)
C2–N3–C9	106.6(3)	C17–N16–Pb	94.1(2)
C2–N3–C17	121.4(3)	N3–C17–N16	121.0(3)
C9–N3–C17	132.0(3)	N3–C17–S18	119.8(3)
C7–C8–N1	128.7(5)	S18–Pb–C20	105.6(1)
N1–C8–C9	111.9(4)	N16–Pb–C20	87.3(1)
N3–C9–C8	103.7(4)	Pb–C20–C21	119.2(3)
N3–C9–C4	133.7(4)	Pb–C20–C25	121.0(3)
N16–C17–S18	119.2(3)	O26–Pb–S18	140.1(1)
C17–S18–Pb	89.1(1)	O26–Pb–C20	72.9(1)
S18–Pb–N16	57.54(7)	C20–Pb–C20	145.8(1)

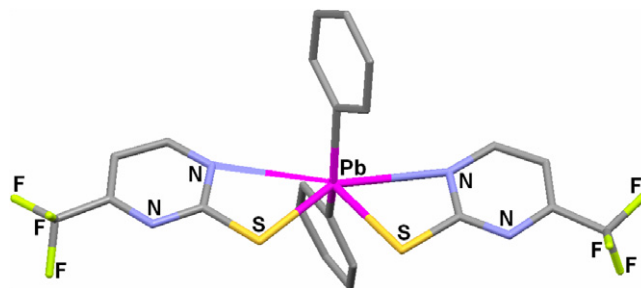


Fig. 11. Distorted geometry in a reported hexacoordinated lead compound [22]. Angles values are N–Pb–N 161.9°, S–Pb–S 83.96° and C–Pb–C 142.8°.

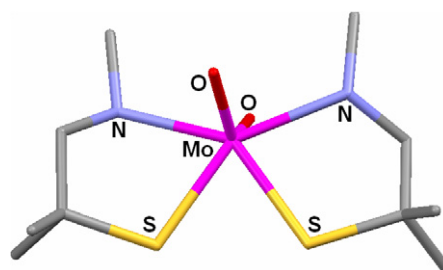


Fig. 12. Hexacoordinate dioxomolybdenum(VI) complexes containing a non-octahedral, *cis-mer* structure presenting a short $S \cdots S$ contact [33].

lead compounds were coordinated by Lewis bases, which approach the metal atom from a direction opposed to the S–M bond through the cavity formed by the *M*-phenyl groups. In some crystals a

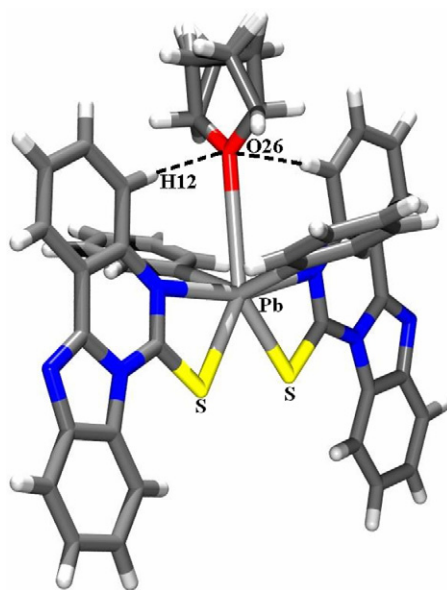


Fig. 13. Solid state structure of compound **5(THF)** showing the two hydrogen bonds to the THF oxygen atom (2.545 Å).

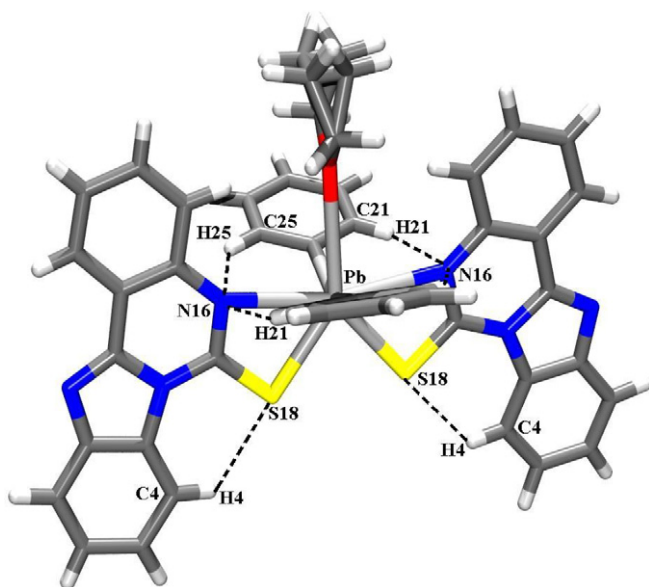


Fig. 14. Solid state structure of **5(THF)** showing the N16...H25 (2.46 Å, N16-H25-C25 = 135.6°), N16...H21 (2.47 Å, N16-H21-C21 = 140.1°) and S18...H4 (2.636 Å) hydrogen bonds.

solvent molecule was included in the cavity formed by two organometallic molecules. A heptacoordinated diphenyl lead compound having the less common pentagonal bipyramidal geometry was obtained. The isomer formed is the *cis-mer*, with the sulfur atoms lying very close together and stabilized by S...S interaction.

4. Experimental

4.1. General comments

Vacuum line techniques were employed for all manipulations of air and moisture sensitive compounds. THF was dried by distillation from sodium-benzophenone under a nitrogen atmosphere prior to use. Dry CDCl_3 , $\text{DMSO-}d_6$, $\text{THF-}d_8$, SnPh_3Cl and PbPh_3Cl

were purchased from Aldrich and used without further purification, PbPh_2Cl_2 was synthesized according to the literature [34]. The melting points were obtained on a Mel-Temp II apparatus and are uncorrected. Mass spectra in the EI mode were recorded at 20 eV on a Hewlett-Packard HP 5989 spectrometer. High resolution mass spectra were obtained by LC/MSD TOF on an Agilent Technologies instrument with APCI as ionization source. Elemental analyses were performed on Eager 300 equipment. ^1H , ^{13}C [ε 25.145020, $\text{Si}(\text{CH}_3)_4$], ^{15}N [ε 10.136767, CH_3NO_2], ^{119}Sn [ε = 37.290 $\text{Sn}(\text{CH}_3)_4$] and ^{207}Pb [ε 20 920 597, $\text{Pb}(\text{CH}_3)_4$]. ^{15}N spectra were obtained with single pulse experiments, whereas ^{119}Sn and ^{207}Pb were obtained by single pulse with broad decoupling experiments. NMR spectra were obtained on a Jeol GSX-270, Jeol Eclipse 400 MHz and Bruker Advance 300 MHz. IR spectra were taken in KBr disc using a FT Spectrum GX Perkin-Elmer spectrometer.

4.2. Syntheses

4.2.1. 5H-benzimidazo[1,2-c]quinazoline-6-thione (**1**)

2-(1H-benzimidazol-2-yl)-phenylamine (500 mg, 2.39 mmol) was reacted with KOH (268 mg, 4.78 mmol) in DMF (20 mL). The solution was stirred for 2 h, then cooled to 0 °C and an excess of CS_2 (11.6 mmol, 0.7 mL) was added and stirred for another 2 h. The reaction mixture was neutralized with aqueous HCl, filtered and washed with CHCl_3 . The product is a light brown powder. Light brown plates were obtained by recrystallization from CHCl_3 (570 mg, 95%). M.p. 284–285 °C. ^1H NMR ($\text{DMSO-}d_6$), δ (ppm): 13.45 (s, N-H), 9.35 (d, 3J 8.3 Hz, H-4), 8.33 (d, 3J 7.9 Hz, H-15), 7.87 (d, 3J 7.9 Hz, H-7), 7.67 (t, 3J 7.9 Hz, H-13), 7.54 (t, 3J 7.9 Hz, H-6), 7.45 (dd, 3J 7.9, 8.3 Hz, H-5), 7.43 (t, 3J 7.9 Hz, H-14), 6.88 (d, 3J 7.9 Hz, H-12). ^{13}C NMR ($\text{DMSO-}d_6$), δ (ppm): 169.2 (C17), 145.1 (C2), 144.2 (C8), 135.6 (C11), 132.4 (C13), 132.1 (C9), 125.9 (C6), 125.0 (C14), 124.3 (C15), 123.2 (C5), 119.2 (C7), 116.9 (C4), 115.9 (C12), 113.2 (10). ^{15}N NMR ($\text{DMSO-}d_6$), δ (ppm): -225.6 (1J 93.6 Hz, N16), -195.6 (N3), -146.3 (N1). EM: m/z (%): 251(100) $[\text{M}]^+$, 219(8.0) $[\text{M-S}]^+$, 207(6.0) $[\text{M-CS}]^+$. Anal. Calc. for $\text{C}_{14}\text{H}_9\text{N}_3\text{S}$: C, 66.91; H, 3.61; N, 16.72. Found: C, 66.59; H, 3.66; N, 16.76%. IR (KBr), ν (cm^{-1}): 1633 (C=N), 1326 (C-N), 1176 (C=S), 3464 (N-H). A polymorph of **1** was obtained from recrystallization in acetone, as light brown plates. M.p. 298 °C. EM: m/z (%): 251(100) $[\text{M}]^+$, 219(36) $[\text{M-S}]^+$, 207(28) $[\text{M-CS}]^+$. Anal. Calc. for $\text{C}_{14}\text{H}_9\text{N}_3\text{S}$: C, 66.91; H, 3.61; N, 16.72. Found: C, 66.58; H, 3.98; N, 16.52%. IR (KBr), ν (cm^{-1}): 1628 (C=N), 1324 (C-N), 1168 (C=S), 3454 (N-H).

4.2.2. (Benzimidazo[1,2-c]quinazoline- κN)-6-thiolate- κS]triphenyl tin (**3**) $^1J\{^{119}\text{Sn}-^{13}\text{C}\}$

Compound **1** (86 mg, 34 mmol) was dissolved in THF and 8.2 mg (34 mmol) of NaH was added. The solution was cooled to -70 °C and $(\text{C}_6\text{H}_5)_3\text{SnCl}$ (132 mg, 34 mmol) was added and the reaction mixture stirred for 15 h at r.t., then filtered and the solvent evaporated under vacuum. A light brown powder was obtained (175 mg, 85%). M.p. 298–300 °C. ^1H NMR (CDCl_3), δ (ppm): 8.86 (d, 3J 8.2 Hz, H-4), 8.63 (d, 3J 7.4 Hz, H-15), 8.02 (d, 3J 8.0 Hz, H-7), 7.59 (H-6), 7.56 (H-13), 7.52 (H-5), 7.50 (H-14), 7.29 (d, 3J 8.1 Hz, H-12). ^{13}C NMR (CDCl_3), δ (ppm): 152.5 (C17), 147.7 (C2), 144.3 (C8), 142.2 (C11), 140.0 ($^1J\{^{119}\text{Sn}-^{13}\text{C}\}$ 606.0 and $^1J\{^{117}\text{Sn}-^{13}\text{C}\}$ 579.1 Hz, C_i), 136.6 ($^1J\{^{119}\text{Sn}-^{13}\text{C}\}$ 46.5 Hz, C_o), 131.8 (C13), 130.2 (C9), 129.9 ($^1J\{^{119}\text{Sn}-^{13}\text{C}\}$ 13.1 Hz, C_p), 129.1 ($^1J\{^{119}\text{Sn}-^{13}\text{C}\}$ 62.0 Hz, C_m), 126.6 (C14), 126.0 (C6), 124.6 (C12), 124.5 (C15), 123.1 (C5), 119.8 (C7), 117.2 (C10), 115.6 (C4). ^1H NMR ($\text{DMSO-}d_6$), δ (ppm): 9.23 (H-4), 8.35 (H-15), 7.85 (H-7), 7.50 (H-6), 7.62 (H-13), 7.44 (H-5), 7.41 (H-14), 7.48 (H-12). ^{13}C NMR ($\text{DMSO-}d_6$), δ (ppm): 159.1 (C17), 147.0 (C2), 143.7 (C8), 141.7 (C11), 143.5 ($^1J\{^{119}\text{Sn}-^{13}\text{C}\}$ 766.0 and $^1J\{^{117}\text{Sn}-^{13}\text{C}\}$

732.2 Hz, C₁), 136.0 (²J{¹¹⁹Sn–¹³C} 45.5 Hz, C_o), 131.5 (C13), 130.7 (C9), 128.9 (C_p), 128.4 (³J{¹¹⁹Sn–¹³C} 67.7 Hz, C_m), 124.8 (C14), 125.0 (C6), 123.4 (C12), 123.6 (C15), 121.9 (C5), 118.8 (C7), 115.4 (C10), 116.7 (C4). IR (KBr), ν (cm⁻¹): 1625 (C=N), 1347 (C–N), 697 (C–S). EM: *m/z* (%): 601(2.9) [M]⁺, 524(100) [M–C₆H₅]⁺, 251(98.7) [M–Sn(C₆H₅)₃]⁺. Anal. Calc. for C₃₂H₂₃N₃SnS: C, 64.03; H, 3.86; N, 7.00. Exp.: C, 63.86; H, 3.95; N, 6.89%.

4.2.3. (Benzimidazo[1,2-*c*]quinazoline-κN)-6-thiolate-κS]triphenyl lead (4)

Compound **1** (400 mg, 1.59 mmol) was dissolved in 30 mL of THF, 42 mg (1.75 mmol) of NaH were added followed by (C₆H₅)₃PbCl (754 mg, 1.59 mmol). The reaction mixture was stirred for 3 days at r.t., then filtered and the solvent evaporated under vacuum. A light brown powder was obtained (850 mg, 77%). M.p. 290 °C. ¹H NMR (CDCl₃), δ (ppm): 9.01 (H-4), 8.63 (H-15), 8.07 (H-7), 7.55 (H-6), 7.58 (H-13), 7.47 (H-5), 7.50 (H-14), 7.36 (H-12). ¹³C NMR (CDCl₃), δ (ppm): 153.1 (C17), 147.6 (C2), 143.8 (C8), 142.3 (C11), 156.5 (¹J{²⁰⁷Pb–¹³C} 553.5 Hz, C₁), 136.5 (¹J{²⁰⁷Pb–¹³C} 84.6 Hz, C_o), 131.2 (C13), 130.2 (C9), 129.9 (¹J{²⁰⁷Pb–¹³C} 123.1 Hz, C_m), 129.3 (¹J{²⁰⁷Pb–¹³C} 22.7 Hz, C_p), 125.7 (C14), 125.2 (C6), 124.6 (C12), 124.0 (C15), 122.3 (C5), 119.2 (C7), 116.7 (C10), 115.9 (C4). ¹H NMR (DMSO-*d*₆), δ (ppm): 9.23 (H-4), 8.35 (H-15), 7.85 (H-7), 7.50 (H-6), 7.62 (H-13), 7.48 (H-12), 7.44 (H-5), 7.41 (H-14). ¹³C NMR (DMSO-*d*₆), δ (ppm): 160.3 (C17), 160.3 (¹J{²⁰⁷Pb–¹³C} 754.7 Hz, C₁), 146.9 (C2), 143.7 (C8), 141.3 (C11), 136.2 (¹J{²⁰⁷Pb–¹³C} 83.3 Hz, C_o), 131.7 (C13), 130.4 (C9), 129.8 (¹J{²⁰⁷Pb–¹³C} 109.1 Hz, C_m), 129.6 (¹J{²⁰⁷Pb–¹³C} 23.3 Hz, C_p), 125.4 (C6), 125.2 (C14), 123.7 (C15), 122.2 (C12, C5), 119.0 (C7), 116.6 (C4), 115.6 (C10). TOF-MS: [M+H]⁺. Calc. for C₃₂H₂₄N₃SPb: 690.1457 a.m.u. Exp.: 690.1451 a.m.u. (Error = 4.94 ppm).

4.2.4. Bis[(benzimidazo[1,2-*c*]quinazoline-κN)-6-thiolate-κS]diphenyl lead (5)

To a solution of compound **1** (300 mg, 1.2 mmol) in 30 mL of THF, 33 mg (1.38 mmol) of NaH were added. Then (C₆H₅)₂PbCl₂ (258 mg, 0.60 mmol) was added and the reaction mixture was stirred for 3 days at r.t., then filtered and the solvent evaporated under vacuum. A colorless powder was obtained (375 mg, 73%). Dec. at 300 °C. ¹H NMR (DMSO-*d*₆), δ (ppm): 9.47 (H-4), 8.38 (H-15), 7.82 (H-7), 7.68 (H-13), 7.48 (H-12), 7.45 (H-14), 7.40 (H-6), 7.36 (H-5). ¹³C NMR (DMSO-*d*₆), δ (ppm): 173.4 (¹J{²⁰⁷Pb–¹³C} 1729.3 Hz, C₁), 165.2 (C17), 147.2 (C2), 143.9 (C8), 142.9 (C11), 132.7 (¹J{²⁰⁷Pb–¹³C} 120.4 Hz, C_o), 131.5 (C13), 131.1 (C9), 129.4 (¹J{²⁰⁷Pb–¹³C} 209.7 Hz, C_m), 128.8 (¹J{²⁰⁷Pb–¹³C} 41.5 Hz, C_p), 124.7 (C6), 123.8 (C15, C12), 123.6 (C14), 121.3 (C5), 118.4 (C7), 117.3 (C4), 115.4 (C10). IR (KBr), ν (cm⁻¹): 1622 (C=N), 1346 (C–N), 686 (C–S). TOF-MS: [M+Na–THF]⁺. Calc. C₄₀H₂₆N₆S₂PbNa: 885.1319 a.m.u. Exp.: 885.1163 a.m.u. (Error = 0.34 ppm). Anal. Calc. for: C₄₄H₃₄N₆PbS₂ · C₄ H₈O · H₂O: C, 48.06; H, 3.70; N, 7.01. Exp.: C, 47.82; H, 3.40; N, 7.01.

4.3. Crystallographic study

Data were measured on a Nonius Kappa CCD instrument with a CCD area detector using graphite-monochromated MoKα radiation. Intensities were measured using φ + ω scans. Crystals obtained from CDCl₃ (**1a**) and acetone (**1b**). Compounds **3** and **4** crystallized from CDCl₃, both co-crystallized with a solvent molecule. Crystals from DMSO (**3e**), DMSO–THF 1/10 (**3a**), THF (**3c** and **5**) and acetone (**3d**) were obtained. All structures were solved using direct methods, using SHELX-97 [35] and the refinement (based on *F*² of all data) was performed by full-matrix least-squares techniques with Crystals 12.84 [36].

All non-hydrogen atoms were refined anisotropically. For **1a**–**1b**, **3b**–**3e** and **5** all hydrogen atoms were located using a difference map, except those of the disordered solvent molecules which were geometrically placed. For **1a** and **1b** only the NH positions were refined, the rest were included as riding atoms. The position of the hydrogen atoms in **3a** and **3b** were refined whereas in **3d**, **3e** and **4** the hydrogen atoms were replaced in ideal positions and included as riding atoms. In compound **5** only the positions of all aromatic hydrogens were refined. Selected bond lengths and angles are presented in Table 3.

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Supplementary material

CCDC 683576, 683577, 683578, 683579, 683580, 683581, 683582, 683583 and 683584 contain the supplementary crystallographic data for **1a**, **1b**, **3a**, **3b**, **3c**, **3d**, **3e**, **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.05.022.

References

- [1] M.F. Braña, M.J. Pérez de Vega, D. Perron, D. Conlon, P.F. Bousquet, S.P. Robinson, *J. Heterocyclic Chem.* 34 (1997) 807.
- [2] R. Rastogi, S. Sharma, *Ind. J. Chem.* 20B (1981) 579.
- [3] B.M. Fernández, J.M. Castellano, M.C. Redondo, E. Schlick, G. Keilhauer, *Eur. Patent Appl.*, 1989, EP0331093.
- [4] G.B. Barlin, S.J. Ireland, *Aust. J. Chem.* 38 (1985) 1685.
- [5] D.R. Williams, *Chem. Rev.* 72 (1972) 203.
- [6] E.S. Raper, *Coord. Chem. Rev.* 61 (1985) 115.
- [7] E.S. Raper, *Coord. Chem. Rev.* 153 (1996) 199.
- [8] R. Contreras, V.M. Jiménez-Pérez, C. Camacho-Camacho, M. Güizado-Rodríguez, B. Wrackmeyer, *J. Organomet. Chem.* 604 (2000) 229.
- [9] V.M. Jiménez-Pérez, C. Camacho-Camacho, M. Güizado-Rodríguez, H. Nöth, R. Contreras, *J. Organometal. Chem.* 614/615 (2000) 283.
- [10] V.M. Jiménez-Pérez, A. Ariza-Castolo, A. Flores-Parra, R. Contreras, *J. Organometal. Chem.* 691 (2006) 1584.
- [11] A. Peña-Hueso, A. Esparza-Ruiz, I. Ramos-García, A. Flores-Parra, R. Contreras, *J. Organometal. Chem.* 693 (2008) 492.
- [12] P. Molina, M. Alajarín, A. Vidal, *Tetrahedron* 45 (1989) 4263.
- [13] L.R. Hughes, J. Oldfield, H. Tucker, *Eur. Patent* (1985) Appl., 1985, EP0154528.
- [14] A.L.L. Poot, J.F. Willems, F.C. Heugebaert, *Bull. Soc. Chim. Belg.* 72 (1963) 365.
- [15] T. Nishio, M. Fujisawa, Y. Omote, *J. Chem. Soc. Perkin Trans. I* (1987) 2523.
- [16] R.H. Bahekar, A.R.R. Rao, *Ind. J. Heterocyclic Chem.* 8 (1999) 225.
- [17] M. Soukri, G. Guillaumet, T. Besson, D. Aziane, M. Aadil, E.M. Essassi, M. Akssira, *Tetrahedron Lett.* 41 (2000) 5857.
- [18] A. Ivachtchenko, S. Kovalenko, O. Drushlyak, *Heterocyclic Commun.* 8 (2002) 233.
- [19] M. Witanowski, L. Stefaniak, G.A. Webb, *Ann. Rep. NMR Spectrosc.* 25 (1993) 2. 225.
- [20] C.V. Rodarte de Moura, A.P.G. de Sousa, R.M. Silva, A. Abras, M. Hörner, A.J. Bortoluzzi, C.A.L. Filgueiras, J.L. Wardell, *Polyhedron* 18 (1999) 2961.
- [21] C.-L. Ma, Y. Shi, Q.F. Zhang, Q. Jiang, *Polyhedron* 24 (2005) 1109.
- [22] A. Rodriguez, A. Sousa-Pedraes, J.A. García-Vázquez, J. Romero, A. Sousa, U. Russo, *Eur. J. Inorg. Chem.* (2007) 1444.
- [23] J.S. Casas, E.E. Castellano, J. Ellena, M.S. García-Tasende, A. Sánchez, J. Sordo, A. Touceda-Varela, *Inorg. Chem. Commun.* 7 (2004) 1109.
- [24] M.D. Couce, V. Cherchi, G. Faraglia, U. Russo, L. Sindellari, G. Valle, N. Zancan, *Appl. Organomet. Chem.* 10 (1996) 35.
- [25] M.N. Xanthopoulou, S.K. Hadjidakou, N. Hadjiliadis, M. Kubicki, S. Karkabounas, K. Charalabopoulos, N. Kourkoumelis, T. Bakas, *J. Organomet. Chem.* 691 (2006) 1780.
- [26] J. Holecck, M.M. Nadvornik, K.J. Handlir, *Organometal* 241 (1983) 177.
- [27] S.S. Batsanov, *Inorg. Mater.* 37 (2001) 1031.
- [28] M. Kaupp, *Angew. Chem., Int. Ed.* 40 (2001) 3534.
- [29] K.A. Singh, V.D. Gupta, G. Linti, H. Nöth, *Z. Naturforsch.* 47b (1992) 1154.
- [30] R. Schmiedgen, F. Huber, H. Preut, *Acta Crystallogr., Sect. C, Cryst. Struct. Commun.* 49 (1993) 1735.

- [31] S.K. Hadjikakou, M.A. Demertzi, M. Kubicki, D. Kovala-Demertzi, *Appl. Organomet. Chem.* 14 (2000) 727.
- [32] C.L. Ma, J. Sun, Y. Shi, R. Zhang, *J. Organomet. Chem.* 690 (2005) 1560.
- [33] J.M. Berg, D.J. Spira, K.O. Hodgson, A.E. Bruce, K.F. Miller, J.L. Corbin, E.I. Stiefel, *Inorg. Chem.* 23 (1984) 3412.
- [34] H. Gilman, J.D. Robinson, *J. Am. Chem. Soc.* 51 (1929) 3112.
- [35] G.M. Sheldrick, *SHELX-97-2 Users Manual*, University of Göttingen, Germany, 1977.
- [36] P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, *J. Appl. Crystallogr.* 36 (2003) 1487.