

Diphenyllead(IV) Chloride Complexes with Benzilthiosemicarbazones. The First Bis(Thiosemicarbazone) Derivatives

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Reactions of diphenyllead(IV) chloride with benzil bis(thiosemicarbazone) (L^1H_6) and benzil bis(4-methyl-3-thiosemicarbazone) ($L^1Me_2H_4$) afforded the first complexes containing the diphenyllead(IV) moiety with bis(thiosemicarbazone) ligands. The new complexes show diverse structural characteristics depending on the ligand and the working conditions. Complexes $[PbPh_2Cl(L^1H_5)] \cdot 3H_2O$ (**1**) and $[PbPh_2Cl(L^1Me_2H_3)]$ (**3**) are mononuclear species in which the ligands are partially deprotonated and the lead atom has a $C_2N_2S_2Cl$ environment in a distorted pentagonal bipyramid coordination geometry. Complex $[PbPh(L^1Me_2H_2)]_2 \cdot 2H_2O$ (**4**) was also obtained, which contains two lead atoms in a binuclear structure with a $C_2N_2S_3$ coordination sphere for each lead atom, since both dideprotonated ligands act as N_2S_2 chelate and as sulfur bridge. Reaction from L^1H_6 , in the same conditions in which complex **4** was prepared, gave a mixture of products: the lead (II) complex $[Pb(L^1H_4)]_2$ (**2**) and $[PbPh_3Cl]_n$. Reactions with the cyclic molecules 5-methoxy-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]-triazine-3-thione ($L^2H_2OCH_3$) and 5-methoxy-4-methyl-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]-triazine-3-thione ($L^2MeHOCH_3$) were also explored. In all the complexes, the ligands are deprotonated. The complexes $[PbPh_2(L^2)]_2$ (**5**) and $[PbPh_2(L^2MeOCH_3)_2]$ (**7**) present the same characteristics. The X-ray structure of **5** shows a distorted octahedral geometry around the lead atom, with the ligand molecules acting as NS chelates, but the nitrogen bonded to the metal is different; one of the triazines shows a novel behavior, since the nitrogen atom of the new imine group formed is the one that is bonded to the lead center, being a good example of linkage isomerism. The complex $[PbPh_2Cl(L^2)]$ (**6**), which was also isolated, could not be crystallized. All the complexes were characterized by elemental analysis, mass spectrometry, IR and 1H , ^{13}C , and ^{207}Pb NMR spectroscopy and some of them by X-ray diffraction studies.

Introduction

The coordination chemistry of diorganolead derivatives has long been known. However, today only a limited number of structures of these complexes have been identified.^{1–4} Lead is one of the most common and important trace metals in the environment; the past massive use of organolead compounds in fuel as antiknock agents and the use of inorganic lead in battery production, have caused a dramatic increase in the presence of this element in the environment.⁵ Furthermore, some evidence for formation of alkyllead

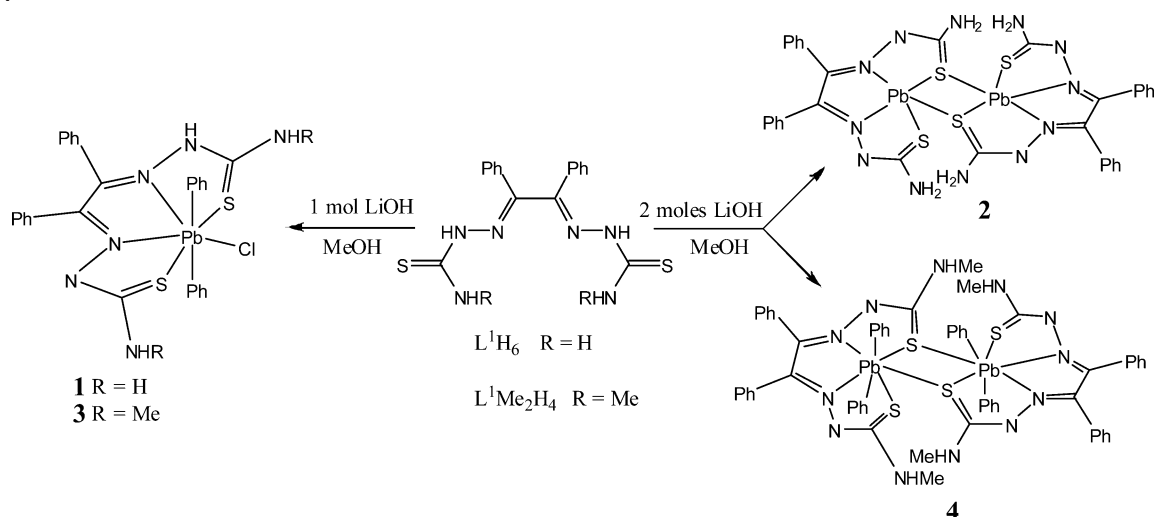
compound in nature from inorganic lead has been described. On the other hand, there is no therapy for organolead poisoning, the chelating agents used to reduce the burden of other heavy metals are not effective against organolead.⁶ Due to its environmental relevance, a renaissance of interest in the coordination chemistry of lead has been observed in recent years.^{7–14} The Pb–C bonds are rather weak, consequently, organolead(IV) halides decompose at room tem-

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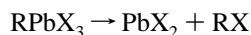
Scheme 1



perature, especially when exposed to light, although aryl derivatives are somewhat more stable than alkyl derivatives.^{1,15} The decomposition of dialkyllead dihalides involves a redistribution reaction,



followed by reductive elimination of RX from the unstable monoorganolead derivative:



These reactions hinder the synthesis of diorganolead(IV) complexes with anionic ligands; reactions with soft anionic ligands lead very often to Pb(II) and $R_3Pb(IV)$ complexes instead of to the diorganolead(IV) derivative.^{14,16}

Following our interest in the coordination chemistry of ligands derived from thiosemicarbazides with toxic metals ions, we have explored the interaction of diphenyllead(IV) chloride with ligands derived from thiosemicarbazide and 4-methyl-3-thiosemicarbazide with benzil: The bis(thiosemicarbazones) L^1H_6 and $L^1Me_2H_4$ and the cyclic molecules $L^2H_2OCH_3$ and $L^2MeHOCH_3$ (Schemes 1 and 2). In previous works, we have established the versatile behavior of L^1H_6 , which depends on the working conditions and the coordination preferences of the metal ions. In particular, L^1H_6 acts, at least, as a N_2S_2 chelate and the complexes show different grade of deprotonation, as well as a variety of structures. Moreover, it can also act as bridge through a sulfur atom yielding a dimer and even as chelate and bridge via a nitrogen

atom provided by one terminal amine in a coordination polymer.^{17,18} In the methylmercury derivative, it shows an original behavior, because it is only bonded to the metal ions through the sulfur atoms in a binuclear structure.¹⁹ However, the cyclic molecule $L^2H_2OCH_3$ always acts as a monoanion; in most of the complexes, it acts as an NS chelate and even as bridge through the sulfur atom.^{20,21} As monodentate through the sulfur atom has only been observed in the mercury complexes.²² Moreover, the cyclic ligands are unsymmetrical ambidentate system and can therefore, give rise to linkage isomerism when they are coordinated in some of the mentioned ways, but in the dimethyltin(IV) complex $[SnMe_2(L^2)_2]$, both ligands are bonded by the sulfur and amine nitrogen atoms.²³ In this paper we report the structural characterization of compounds formed by reaction of thiosemicarbazone and 4-methyl-3-thiosemicarbazone derivatives of benzil with diphenyllead(IV) chloride.

As far as we know, the reactions between $PbPh_2Cl_2$ and thiosemicarbazones have only been previously investigated using those [1+1] condensation products.^{11,12} We present in this work the first complexes derived from bis(thiosemicarbazones). The new complexes were characterized by elemental analysis, mass spectrometry, IR and 1H , ^{13}C , and ^{207}Pb NMR spectroscopy and some of them by X-ray diffraction studies.

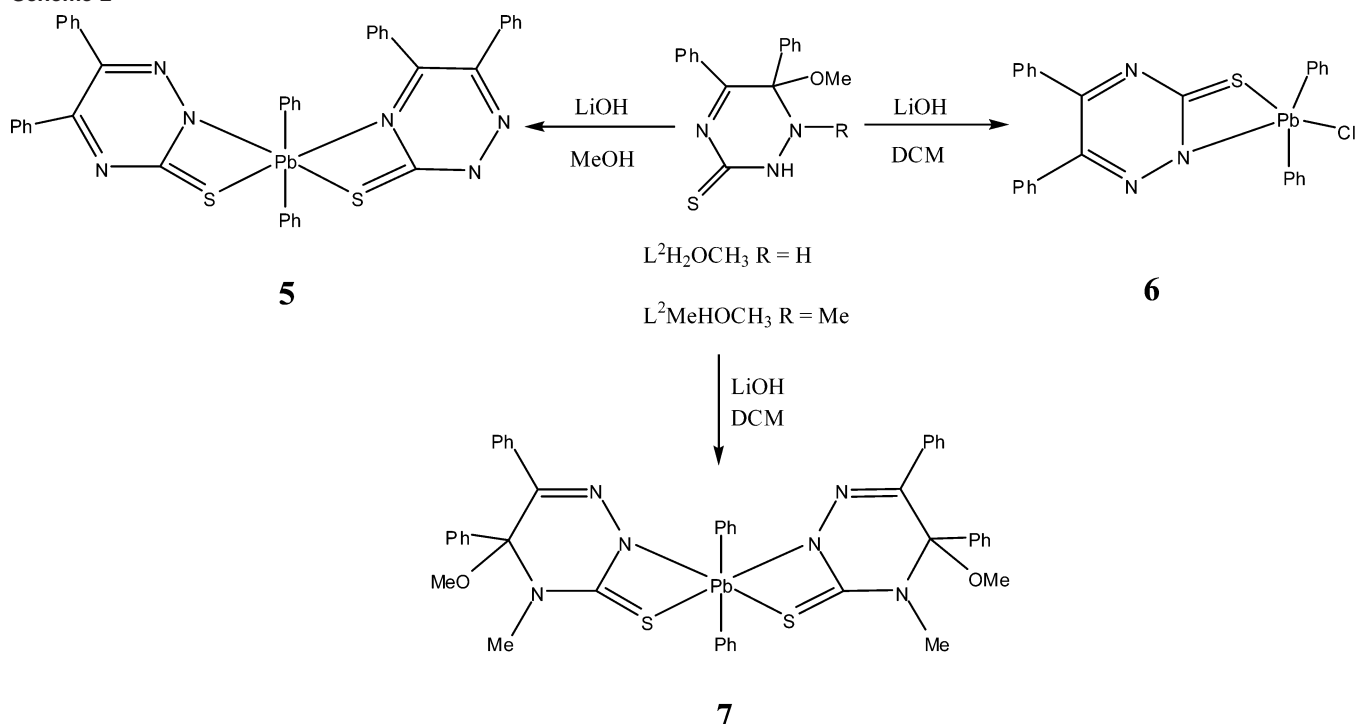
Experimental Section

Physical Measurements. Microanalyses were carried out using a Perkin-Elmer 2400 II CHNS/O Elemental Analyzer. IR spectra in the 4000–400 cm^{-1} range were recorded as KBr pellets on a

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Scheme 2



Jasco FT/IR-410 spectrophotometer. Fast atom bombardment mass spectra were recorded on a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzylalcohol (*m*NBA) as the matrix. 1H and ^{13}C NMR spectra were recorded on a spectrometer Bruker AMX-300 using $CDCl_3$, CD_2Cl_2 , and $DMSO-d_6$ as solvents and TMS as internal reference. ^{207}Pb NMR spectra were recorded in the same spectrometer using $CDCl_3$ and $DMSO-d_6$ as solvents and using absolutes references.²⁴ ^{13}C CP/MAS NMR spectra were recorded at 298 K in a Bruker AV400WB spectrometer equipped with a 4 mm MAS NMR probe (magic-angle spinning) and obtained using cross-polarization pulse sequence. The external magnetic field was 9.4 T, and the sample was spun at 10–14 kHz, spectrometer frequencies were set to 100.61 MHz. For the recorded spectra a contact time of 4 ms were used and recycle delays of 4 s were used. Chemical shifts are reported relative to TMS, using the CH group of adamantano as a secondary reference (29.5 ppm).²⁵

Synthesis. All reagents were obtained from standard commercial sources and were used as received. Methanol, dried Scharlau (max 0.005% H_2O), and dried dichloromethane by refluxing with CaH₂ were used as solvents.

Benzil Bis(thiosemicarbazone), L^1H_6 . It was prepared following the procedure previously reported.¹⁷ Selected spectroscopic data: FAB⁺ (*m/z*): 357 ([M + 1]⁺, 100%), 714 ([2M + 1]⁺, 25%). 1H NMR ($DMSO-d_6$, 300 MHz, 25 °C): δ 9.8 (2H, NH, s), 8.6 (2H, NH₂, s), 8.3 (2H, NH₂, s), 7.7 (4H, Ph, m), 7.4 (6H, Ph, m). 1H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 8.8 (2H, NH, s), 7.6 (6H, Ph, m), 7.4 (4H, Ph, m), 6.6 (2H, NH₂, s), 6.0 (2H, NH₂, s). ^{13}C NMR ($DMSO-d_6$, 300 MHz, 25 °C): δ 179.1 (CS), 140.5 (CN), 133.1, 130.1, 128.9, 126.8 (Ph). ^{13}C CP/MAS NMR (300 MHz, 25 °C): δ 181.1 (CS), 142.9 (CN), 133.3, 132.4 130.1 (Ph). IR (KBr, cm^{-1}): 3420, 3386, 3342, 3330, 3210, 3151(s) [$\nu(NH)$], 1608(w) [$\nu(CN)$], 1581(s) [$\delta(NH_2)$] and 848(w) [$\nu(CS)$].

Benzil Bis(4-methyl-3-thiosemicarbazone),²⁶ $L^1Me_2H_4$. A solution of benzil (Bz) (1.503 g, 7.15 mmol) and 10 drops of HCl (concd) in dry methanol (75 mL) was added to a solution of 4-methyl-3-thiosemicarbazide (4-MeTSC) (1.504 g, 14.30 mmol) in dry methanol (125 mL) and HCl (concd) (1 mL). The solution was stirred under reflux for 45 min. After cooling to room temperature, the pale yellow precipitate formed was filtered off, washed (cold dry methanol), and dried in vacuo. Yield 60%. Mp 224 °C. FAB⁺ (*m/z*): 385.2 ([M + 1]⁺, 80%), 769.6 ([2M + 1]⁺, 10%). 1H NMR ($DMSO-d_6$, 300 MHz, 25 °C): δ 9.8 (2H, NH, s), 8.9 (2H, NH, q), 7.7 (4H, Ph, m), 7.4 (6H, Ph, m), 3.0 (6H, CH₃, d). 1H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 8.5 (2H, NH, s), 7.8 (2H, NH, q), 7.7 (4H, Ph, m), 7.3 (6H, Ph, m), 3.3 (6H, CH₃, d). ^{13}C NMR ($DMSO-d_6$, 300 MHz, 25 °C): δ 178.6 (CS), 140.4 (CN), 133.2, 130.3, 129.1, 126.8 (Ph), 31.5 (CH₃); ^{13}C CP/MAS NMR (300 MHz, 25 °C): δ 177.2 (CS), 139.8 (CN), 130.6, 128.1, 124.7 (Ph), 32.1 (CH₃). IR (KBr, cm^{-1}): 3435, 3335(s) [$\nu(NH)$], 1601(w) [$\nu(CN)$], 1546(s) [$\delta(HNC)$], 845(w) [$\nu(CS)$].

5-Methoxy-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]-triazine-3-thione, $L^2H_2OCH_3$.^{27,28} Selected spectroscopic data: FAB⁺ (*m/z*): 266 ([M - OCH₃]⁺, 10%), 298 ([M + 1]⁺, 35%). 1H NMR ($CDCl_3$, 300 MHz 25 °C): δ 9.5 (1H, NH, s), 7.6 (2H, Ph, m), 7.4 (2H, Ph, m), 7.3–7.1 (6H, Ph, m), 6.9 (1H, NH, s), 3.4 (3H, OCH₃, s). ^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C): δ 169.7 (CS), 142.4 (CN), 141.7, 133.7, 129.3, 126.5 (Ph), 83.2 (CNOR₂), 50.7 (OCH₃). ^{13}C CP/MAS NMR (300 MHz, 25 °C): δ 168.4 (CS), 146.0 143.4 (CN), 132.4, 131.3, 129.8, 127.0 (Ph), 85.4 (CNOR₂), 53.4 (OCH₃). IR (KBr, cm^{-1}): 3184(s) and 3131(s) [$\nu(NH)$], 1608(w) [$\nu(CN)$], 1550(s) [$\delta(NCS)$], 846(w) [$\nu(CS)$].

5-Methoxy-4-methyl-5,6-diphenyl-4,5-dihydro-2H-[1,2,4]-triazine-3-thione, $L^2MeHOCH_3$.²⁶ A solution of 4-MeTSC (1.05 g,

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10 mL) in methanol (40 mL), a solution of 2M HCl (40 mL), HCl (concd) (1 mL), and a solution of Bz (2.10 g, 10 mmol) in methanol (200 mL) were added dropwise with strong stirring to 150 mL of methanol. After the completion of the addition of all the reagents, the mixture was stirred for 4 days. The solution was concentrated and a crystalline white solid was formed. The precipitate was filtered off and dried in vacuo. Yield 80%. Mp 136 °C. FAB⁺(*m/z*): 280.2 ([M - OCH₃]⁺, 13%), 312.2 ([M + 1]⁺, 100%), 622.5 ([2M + 1]⁺, 10%). ¹H NMR (DMSO-*d*₆, 300 MHz, 25 °C): δ 12.3 (1H, NH, s), 7.5–7.2 (10H, Ph, m), 3.2 (3H, OCH₃, s), 2.9 (3H, NCH₃, s). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 9.5 (1H, NH, s), 7.6–7.1 (10H, Ph, m), 3.4 (3H, OCH₃, s), 3.1 (3H, NCH₃, s). ¹³C NMR (DMSO-*d*₆, 300 MHz, 25 °C): δ 171.7 (CS), 141.4 (CN), 139.9, 133.7, 129.3, 128.8, 128.3, 127.9, 126.8, 126.4 (Ph), 87.1 (CNOR₂), 51.1 (OCH₃), 33.3 (NCH₃). ¹³C CP/MAS NMR (300 MHz, 25 °C): δ 173.1 (CS), 146.1 (CN), 140.4, 135.1, 129.4, 126.8, 126.6 (Ph), 87.8 (CNOR₂), 52.0 (OCH₃), 37.1 (CH₃). IR (KBr, cm⁻¹): 3229(s) [ν(NH)], 1612(w) [ν(CN)], 1511(s) [δ(NCS)], 845(w) [ν(CS)].

Synthesis of the Complexes. The complexes were obtained by reacting PbPh₂Cl₂ and each ligand in dry methanol or dried dichloromethane and in the presence of LiOH·H₂O. In every case, a 1:1 mole ratio was used. In the reactions with the bis-(thiosemicarbazones), 1:1 and 1:2 ligand/LiOH·H₂O mole ratios were used.

Caution! Lead is a highly toxic cumulative poison, and lead compounds should be handled carefully.⁶

[PbPh₂Cl(L¹H₅)]·3H₂O (1). To a solution of L¹H₆ (75 mg, 0.21 mmol) and LiOH·H₂O (9 mg, 0.21 mmol) in methanol (20 mL) was added a suspension of diphenyllead(IV) chloride (91 mg, 0.21 mmol) in methanol (10 mL). The mixture was stirred for 4 h, and then the scarce solid was filtered off and dried in vacuo. From the filtrate, yellow crystals suitable for X-ray analysis were obtained. Yield 74%. Mp 197 °C. Anal. Calcd for PbC₂₈H₃₁N₆S₂ClO₃: C, 41.70 H, 3.72; N, 10.42; S, 7.94. Found: C, 42.03; H, 3.76; N, 10.47; S, 7.87. FAB⁺(*m/z*): 563.1 ([Pb(L¹H₅)]⁺, 75%), 639.1 ([PbPh(L¹H₅)]⁺, 25%), 717.2 ([PbPh₂(L¹H₅)]⁺, 20%), 753.1 ([M + 1]⁺, 5%). ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ 9.1 (1H, NH, s), 8.2–6.9 (20H, Ph, m), 6.3 (4H, NH, s). ¹³C NMR (DMSO-*d*₆, 300 MHz, 25 °C): δ 179.5 (CS), 141.0 (CN), 134.3, 133.6, 130.7, 129.3, 127.2 (Ph). ²⁰⁷Pb NMR (300 MHz, DMSO-*d*₆, 25 °C): δ -193.3. ¹³C CP/MAS NMR (300 MHz, 25 °C): δ 172.2 (CS), 167.1, 162.5 (Ph), 157.8, 152.2 (CN), 137.8, 133.9, 132.8, 130.9, 129.4, 12.6 (Ph). IR (KBr, cm⁻¹): 3420, 3365, 3343, 3330, 3244, 3151(s) [ν(NH)], 1698, 1607(w) [ν(CN)], 1564, 1507, 1466, 1446(s) [thioamide II], 764(w) [ν(CS)].

This complex was also obtained using DCM as solvent under reflux for 6 h. The yellow solid was collected by filtration and dried in vacuo.

[Pb(L¹H₄)] (2). A solution of L¹H₆ (75 mg, 0.21 mmol) and LiOH·H₂O (18 mg, 0.42 mmol) in methanol (25 mL) was added over a suspension of diphenyllead(IV) chloride (91 mg, 0.21 mmol) in the same solvent (10 mL). The mixture was stirred at room temperature for 4 h. The scarce yellow solid was filtered off and the orange filtrate was partially concentrated until an orange-brown solid (2) was formed. Finally, from the mother liquor afforded a small amount of yellow crystals suitable for X-ray study that turned out to be [PbPh₃Cl]_{*n*}. Data for complex 2: Mp 199 °C (dec). Anal. Calcd for PbC₁₆H₁₄N₆S₂: C, 34.21; H, 2.49; N, 14.97; S, 11.40. Found: C, 34.45; H, 2.69; N, 14.64; S, 11.20. FAB⁺(*m/z*): 563 ([Pb(L¹H₅)]⁺, 5%). ¹³C CP/MAS NMR (300 MHz, 25 °C): δ 175.9 (CS), 154.7, 150.6 (CN), 138.2, 129.5 (Ph). IR (KBr, cm⁻¹): 3443, 3313(s) [ν(N-H)], 1565, 1468, 1437(s) [thioamide II], 768(w)

[ν(CS)]. Data for [PbPh₃Cl]_{*n*}: IR (KBr, cm⁻¹) 3057(m) [ν(CH)], 1597, 1576, 1496, 1486 1476, 1432 [ν(CC)], 757, 750, 731,720, 699, 691, [δ(CH)_{op}].

[PbPh₂Cl(L¹Me₂H₃)] (3). A solution of L¹Me₂H₄ (89 mg, 0.23 mmol) and LiOH·H₂O (10 mg, 0.23 mmol) in methanol (25 mL) was added over a suspension of diphenyllead(IV) chloride (100 mg, 0.23 mmol) in the same solvent (10 mL). The mixture was stirred for 4 h, and then the yellow solid was filtered off and dried in vacuo. Yield 77%. Mp 184 °C. Anal. Calcd for PbC₃₀H₂₉N₆S₂Cl: C, 46.20 H, 3.74; N, 10.80; S, 8.20. Found: C, 45.94; H, 3.72; N, 10.68; S, 8.14. FAB⁺(*m/z*): 590.9 ([Pb(L¹Me₂H₃)]⁺, 30%), 667.0 ([PbPh(L¹Me₂H₃)]⁺, 20%), 745 ([PbPh₂(L¹Me₂H₃)]⁺, 25%), 781.1 ([M + 1]⁺, 5%). ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 8.3 (1H, NH, s), 7.8–6.9 (22H, Ph+NH, m), 3.2 (6H, CH₃, d). ¹³C CP/MAS NMR (300 MHz, 25 °C): δ 177.8, 175.3 (CS), 167.3, 166.1 (PbPh), 146.4 and 145.6 (CN), 134.2, 132.8, 130.7, 129.9, 127.5 (Ph), 31.7 (CH₃). ²⁰⁷Pb NMR (300 MHz, DMSO-*d*₆, 25 °C): δ -196.9. IR (KBr, cm⁻¹): 3386, 3340, 3271(s) [ν(NH)], 1543 and 1475(vs) [thioamide II], 847(w) [ν(CS)].

[PbPh₂(L¹Me₂H₂)₂·2H₂O (4). A solution of L¹Me₂H₄ (89 mg, 0.23 mmol) and LiOH·H₂O (20 mg, 0.48 mmol) in methanol (60 mL) was added over a suspension of diphenyllead(IV) chloride (100 mg, 0.23 mmol) in the same solvent (20 mL). Immediately, an orange solution was formed, and then the solution was stirred for 6 h. An orange solid was separated by slow evaporation of the solvent. Yield 53%. Mp 188 °C (dec). Anal. Calcd for Pb₂C₆₀H₆₀N₁₂S₄O₂: C, 47.29 H, 3.97; N, 11.03; S, 8.42. Found: C, 47.18; H, 3.60; N, 10.92; S, 8.39. FAB⁺(*m/z*): 591.2 ([Pb(L¹Me₂H₃)]⁺, 70%), 667.1 ([PbPh(L¹Me₂H₂)+1]⁺, 60%), 745.1 ([PbPh₂(L¹Me₂H₃)]⁺, 100%), 951.2 ([Pb₂Ph₂(L¹Me₂H₃)]⁺, 13%), 1104.4 ([Pb₂-Ph₄(L¹Me₂H₂)]⁺, 17%). ¹³C CP/MAS NMR (300 MHz, 25 °C): δ 176.9, 174.2, 171.3 (CS), 152.6, 146.3 (CN), 135.3, 132.8, 128.7, 127.7, 124.7, 121.8 (Ph), 28.5 (CH₃). ²⁰⁷Pb NMR (300 MHz, DMSO-*d*₆, 25 °C): δ -610.8. IR (KBr, cm⁻¹) 3424, 3384(s) ν(NH); 1560, 1518(s) [ν(CN)] + [thioamide II], 844, 816(w) [ν(CS)]. Brown-yellow crystals suitable for X-ray diffraction were obtained from the mother liquor.

[PbPh₂(L²)₂] (5). To a solution of L²H₂OCH₃ (100 mg, 0.33 mmol) and LiOH·H₂O (14 mg, 0.33 mmol) in methanol (10 mL) was added a suspension of diphenyllead(IV) chloride (145 mg, 0.33 mmol) in methanol (20 mL). The mixture was stirred for 4 h at room temperature. The yellow solid formed was filtered off, washed with methanol and acetone, and dried in vacuo. Yield 70%. Mp 202 °C. Anal. Calcd for PbC₄₂H₃₀N₆S₂: C, 56.68; H, 3.37; N, 9.44; S, 7.19. Found: C, 56.54; H, 3.36; N, 9.34; S, 7.12. FAB⁺(*m/z*): 266.0 ([L² + 1]⁺, 15%), 470.9 ([Pb(L²)]⁺, 25%), 626 ([PbPh₂(L²)]⁺, 58%), 813 ([M - Ph]⁺, 5%), 891.0 ([M + 1]⁺, 10%). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 7.98 (4H, Ph, d), 7.34 (26H, Ph, m), ³J(²⁰⁷Pb-¹H) = 159.49. ¹³C NMR (CDCl₃, 300 MHz, 25 °C): δ 175.1 (CS), 152.9, 156.2 (CN), 134.3, 131.4, 130.4, 129.7, 128.4 (Ph), ²J(²⁰⁷Pb-¹³C) = 109.50. ²⁰⁷Pb NMR (300 MHz, CDCl₃, 25 °C) δ -211.58. ²⁰⁷Pb NMR (DMSO-*d*₆, 300 MHz, 25 °C): δ -315.30. IR (KBr, cm⁻¹): 1578, 1565(w) [ν(CN)], 1499, 1486(s), [δ(NCS)], 846, 819(w) [ν(CS)]. Recrystallization in acetone gave yellow crystals suitable for X-ray analysis.

[PbPh₂Cl(L²)] (6). To a suspension of L²H₂OCH₃ (100 mg, 0.33 mmol) and LiOH·H₂O (14 mg, 0.33 mmol) in CH₂Cl₂ (20 mL) was added a suspension of diphenyllead(IV) chloride (145 mg, 0.33 mmol) in the same solvent (20 mL). The mixture was stirred under reflux for 12 h. Then, the mixture was filtered off and the filtrate was partially evaporated until a yellow solid was formed. Yield 41%. Mp 105 °C. Anal. Calcd for PbC₂₇H₂₀N₃SCl: C, 49.04; H, 3.03; N, 6.36; S, 4.84. Found: C, 49.47; H, 3.21; N, 6.43; S, 4.90.

Table 1. Crystallographic Data for Complexes

compound	1	4	5
empirical formula	C ₂₈ H ₃₁ ClN ₆ O ₃ PbS ₂	C ₆₀ H ₆₀ N ₁₂ O ₂ Pb ₂ S ₄	C ₄₂ H ₃₀ N ₆ PbS ₂
fw	806.35	1523.88	890.03
T (K)	298(2)	150	100(2)
cryst syst	orthorhombic	monoclinic	monoclinic
space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	17.3952(2)	12.8952(2)	14.0427(9)
<i>b</i> (Å)	18.4260(2)	9.6592(2)	9.7998(6)
<i>c</i> (Å)	18.8946(2)	24.3891(5)	26.4633(18)
α (°)	90	90	90
β (°)	90	103.1671(8)	94.238(2)
γ (°)	90	90	90
<i>V</i> (Å ³)	6056.17(12)	2957.98(10)	3631.8(4)
<i>Z</i>	8	2	4
<i>D</i> _{calcd} (Mg/m ³)	1.769	1.711	1.628
abs coeff (mm ⁻¹)	13.271	5.879	10.416
<i>F</i> (000)	3168	1496	1752
cryst size (mm ³)	0.11 × 0.07 × 0.04	0.12 × 0.12 × 0.28	0.12 × 0.08 × 0.05
GOF on <i>F</i> ²	1.026	1.0618	1.052
reflns collected	56642	33974	34438
independent reflns	5853	7100	6951
[<i>R</i> (int) = 0.0602]		[<i>R</i> (int) = 0.049]	[<i>R</i> (int) = 0.0406]
final <i>R</i> indices	<i>R</i> 1 = 0.0308	<i>R</i> 1 = 0.0313	<i>R</i> 1 = 0.0243
[<i>I</i> > 2 σ (<i>I</i>)]	w <i>R</i> 2 = 0.0714	w <i>R</i> 2 = 0.0357	w <i>R</i> 2 = 0.0588
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0452	<i>R</i> 1 = 0.0528	<i>R</i> 1 = 0.0257
	w <i>R</i> 2 = 0.0793	w <i>R</i> 2 = 0.0462	w <i>R</i> 2 = 0.0596
largest diff. peak and hole (e.Å ⁻³)	1.544 and -0.660	1.270 and -1.340	1.275 and -0.773

FAB⁺ (*m/z*): 266.0 ([L² + 1]⁺, 30%), 472.1 ([Pb(L²)]⁺, 25%), 626.1 ([PbPh₂(L²)]⁺, 40%), 662.1 ([M + 1]⁺, 5%). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.1 (4H, Ph, d), 7.5 (16H, Ph, m), ³J(²⁰⁷Pb-¹H) = 162.1. ¹³C NMR (CDCl₃, 300 MHz, 25 °C): δ 176.4 (CS), 158.5, 153.9 (CN), 136.3, 134.4, 131.9, 131.4, 130.9, 129.8, 28.5 (Ph), ²J(²⁰⁷Pb-¹³C) = 113.92. ¹³C CP/MAS NMR (300 MHz, 25 °C): δ 173.6 (CS), 157.5, 153.2 (CN), 133.6, 128.9 (Ph). ²⁰⁷Pb NMR (CDCl₃, 300 MHz 25 °C): δ -122.49. IR (KBr, cm⁻¹): 1597, 1563(w) [ν (CN)], 1486, 1472 [δ (NCS)], 843, 817(w) [ν (CS)].

[PbPh₂(L²MeOCH₃)₂] (7). A solution of L²MeHOCH₃ (143 mg, 0.46 mmol) and LiOH·H₂O (20 mg, 0.48 mmol) in CH₂Cl₂ (10 mL) was added over a suspension of diphenyllead(IV) chloride (100 mg, 0.23 mmol) in the same solvent (20 mL). The mixture was stirred for 72 h. Then, the solid was filtered off and the filtrate was partially evaporated until a yellow oil was formed. After freezing at -195 °C, a yellow solid was formed. Yield 48%. Mp 106 °C. Anal. Calcd for PbC₄₆H₄₂N₆S₂O₂: C, 56.25; H, 4.31; N, 8.56; S, 6.53. Found: C, 56.51; H, 4.43; N, 8.66; S, 6.59. FAB⁺ (*m/z*): 312.0 ([L²MeHOCH₃ + 1]⁺, 85%), 518.0 ([Pb(L²MeOCH₃)₂]⁺, 10%), 672 ([PbPh₂(L²MeOCH₃)₂]⁺, 100%), 905.0 ([M - Ph]⁺, 10%), 983.1.0 ([M + 1]⁺, 2%). ¹³C CP/MAS NMR (300 MHz, 25 °C): δ 172.3 (CS), 140.5 (CN), 134.9, 128.5 (Ph), 87.8 (CNOR₂), 51.3 (OCH₃), 34.1 (NCH₃). ²⁰⁷Pb NMR (300 MHz, DMSO, 25 °C): δ -771.56. IR (KBr, cm⁻¹) 1615(w) [ν (CN)], 1564(m) [δ (NCS)], 849(w) [ν (CS)].

The reaction was carried out in the same conditions described above but in methanol at room temperature and under reflux. In both cases, there was not reaction and the reagents were recovered.

X-ray Crystallography. Crystal data, experimental details, and refinement results are listed in Table 1. Single crystals of complexes **1** and **4** were isolated from the mother liquor of the reactions, and crystals of **5** were obtained by recrystallization in acetone.

The crystals of compounds **1** and **5** were mounted on a glass fiber and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer with a MAC Science Co., Ltd. rotating anode (Cu K α radiation, λ = 1.54178 Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA. X-ray data were collected with a combination of six runs at different φ and 2θ angles, 3600 frames. The substantial redundancy in data allows

empirical absorption corrections (SADABS)²⁹ to be applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission: 0.534941 for complex **1** and 0.270617 for complex **5**). The unit cell parameters were obtained by full-matrix least-squares refinements of 6865 reflections for complex **1**, and 7488 for complex **5**. The raw intensity data frames were integrated with the SAINT program, which also applied corrections for Lorentz and polarization effects.³⁰

The software package SHELXTL version 6.10 was used for space group determination, structure solution, and refinement.³¹ The structures were solved by direct methods (SHELXS-97),³² completed with difference Fourier syntheses, and refined with full-matrix least-squares using SHELXL-97 minimizing $\omega(F_0^2 - F_c^2)$.^{2,34} Weighted *R* factors (*R*_w) and all goodness of fit, *S*, are based on *F*²; conventional *R* factors (*R*) are based on *F*.³³ All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library. The high quality of the data set allowed that all hydrogen atoms were located by difference maps and refined isotropically in all complexes. The crystal of complex **4** was mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N₂ using an Oxford Cryosystem CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius Kappa CCD diffractometer (graphite-monochromated Mo K α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package.³⁴

The structure of complex **4** was solved using the direct-methods program SIR92b, which located all non-hydrogen atoms of the complex.³⁵ Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.³⁶ Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Examination of a difference Fourier map showed an isolated peak of electron density, assumed to be the O atom of a molecule of water. The NH hydrogen atoms were located in a difference Fourier map and their coordinates and isotropic thermal parameters subsequently refined. CH hydrogen atoms were positioned geometrically after each cycle refinement. The hydrogen atoms of the molecule of water could not be located, presumably as a result of disorder. They have been omitted from the model but included in calculations of the formula weight, etc.

CCDC 631459 for complex **1**, 631460 for complex **4**, and 631458 for complex **5** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (international) +44-123/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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Results and Discussion

Synthesis of the Complexes. All the reactions were performed by mixing a suspension of PbPh_2Cl_2 with a solution of the corresponding ligand in the same solvent in a 1:1 ratio, except the reaction with $\text{L}^2\text{MeHOCH}_3$, in which a 1:2 ratio was necessary. Reactions were carried out in dry methanol or DCM previously dried due to the presence of water in the solvents leading to the partial decomposition of the complexes. The best results were obtained working in the presence of basic media. The variation of the ratio ligand/lithium hydroxide, gave two kind of complexes: working in a 1:1 ratio, complexes **1** and **3** are obtained, in which the monodeprotonated ligand has displaced one of the two chlorides from the coordination sphere of the metal. However, complex **4**, with the ligands acting as dianion by the loss of the two hydrogens of the acidic amine group, is isolated working in a 1:2 ratio. Complexes **1** and **4** are the first diphenyllead(IV) complexes containing a bis(thiosemicarbazone) ligand that have been structurally characterized. The reaction of PbPh_2Cl_2 with L^1H_6 in the presence of 2 mol of $\text{LiOH}\cdot\text{H}_2\text{O}$ gave several compounds. In the first compound formed (**2**), the dideprotonated ligand has displaced both chlorides and the phenyl groups from the coordination sphere of the metal, giving a complex whose empirical formula corresponds to $[\text{Pb}(\text{L}^1\text{H}_4)]$. Its analytical data and spectroscopic characteristics correspond to the complex obtained by reaction of lead (II) nitrate with benzil bis(thiosemicarbazone), whose MALDI spectrum showed a peak at 770.2 amu corresponding to $[\text{Pb}_2(\text{L}^1\text{H}_4)]^+$.³⁷ The crystal structure of the cadmium complex with the same empirical formula consists of a binuclear compound with the ligand acting as N_2S_2 chelate and sulfur bridge.¹⁷ Therefore, the same structure could be expected for the lead complex. From the mother liquor, an unexpected compound without L^1H_6 $[\text{PbClPh}_3]_n$ is isolated. The former seems likely to have been originated from a phenyl transfer, since it is known that the organolead(IV) compounds undergo disproportionation reactions and transfer of the organic group yielding Pb(II) complexes.^{13,33} The phenyl transfer reactions seem to be favored in the presence of basic media and when terminal NH_2 groups are present in the thiosemicarbazone ligand.

In the reactions with the cyclic molecules, the solvent used is an important factor: the analytical data of the two complexes from $\text{L}^2\text{H}_2\text{OCH}_3$ indicate the loss of a methanol molecule, although they show different formula depending on the solvent. In methanol, a 1:2 complex (**5**) is obtained, while working in DCM only one deprotonated ligand has displaced one of the two chlorides from the coordination sphere of the metal, giving a complex whose empirical formula is $[\text{PbPh}_2\text{Cl}(\text{L}^2)]$ (**6**). An even greater importance is observed in the reaction with $\text{L}^2\text{MeHOCH}_3$, which progresses only working in DCM giving complex **7**.

The FAB^+ mass spectra of complexes **1**, **3**, **5**, **6**, and **7** show the molecular mass peaks, which show the appropriate isotope distribution patterns, confirming the proposed formula

and some additional peaks corresponding to different fragments. The spectrum of **2** only shows peaks corresponding to fragments containing lead and the thiosemicarbazone, which confirms the absence of phenyl rings on the coordination sphere of lead and indicates the reduction to lead(II). The spectra of complexes **1** and **3** show the same fragmentation pattern, so they might present similar structures. The same situation is observed in the spectra of complexes **5** and **7**, so very close structures are expected. The FAB^+ mass spectrum of **4** shows a different fragmentation pattern and the molecular mass peak is not observed, but a peak at 1104.4 uma appears corresponding to $[\text{Pb}_2\text{Ph}_4(\text{L}^1\text{Me}_2\text{H})]^+$, which suggests a binuclear structure.

IR Spectroscopy. The Experimental Section lists the main IR bands of the ligands and their complexes. The absence of any bands in the $2600\text{--}2800\text{ cm}^{-1}$ region in all complexes suggests the absence of any thiol tautomer.³⁸ The spectra also show the bands corresponding to the PbPh_2 moieties, except in complex **2**.

In the spectra of complexes from the open-chain ligands (**1–4**), the number of bands corresponding to $\nu(\text{N–H})$ vibrations has decreased owing to deprotonation and displacement, probably due to the intermolecular hydrogen bonding having been modified. The shifts observed in the bands assigned to $\nu(\text{CN})$ and $\nu(\text{CS})$ are consistent with both groups bonded to the lead atom in all the complexes.

In the complexes from the triazine ligands (**5–7**), there are no bands in the $3000\text{--}3300\text{ cm}^{-1}$ region, indicating the absence of N–H bonds. In all the complexes, the coordination through the sulfur atom can be observed in a decrease of the $\nu(\text{CS})$ frequency. In addition, in complexes from $\text{L}^2\text{H}_2\text{OCH}_3$ (**5** and **6**), a new signal attributable to a CN double bond, due to the loss of a methanol molecule in each ligand, is observed in the IR spectra.

NMR Spectroscopy. The ^1H NMR spectra of all the complexes indicate that the ligands are deprotonated. Spectra of complexes **1** and **3** show the loss of one hydrogen atom from one of the acidic amine groups. However, the spectrum of complex **4** agrees with both $\text{L}^1\text{Me}_2\text{H}_4$ molecules being dideprotonated and they have displaced the two chloride atoms from the coordination sphere of each metal. In the ^{13}C NMR spectrum of complex **1**, the signals lie at the same position than in the free L^1H_6 . ^{207}Pb NMR spectra in DMSO of complexes **1** and **3** show one signal at -193.3 and -196.9 ppm, respectively. These values suggest that both complexes have the same coordination number in DMSO solution and they agree with a coordination number lower than six.³⁹ Therefore, some Pb–L bonds could break in DMSO solution. However, the spectrum of complex **4** shows a signal in the range expected for a coordination number of six.⁴⁰

In the ^1H NMR spectrum of complex **5**, there are no signals corresponding to the methoxy group and the N–H ,

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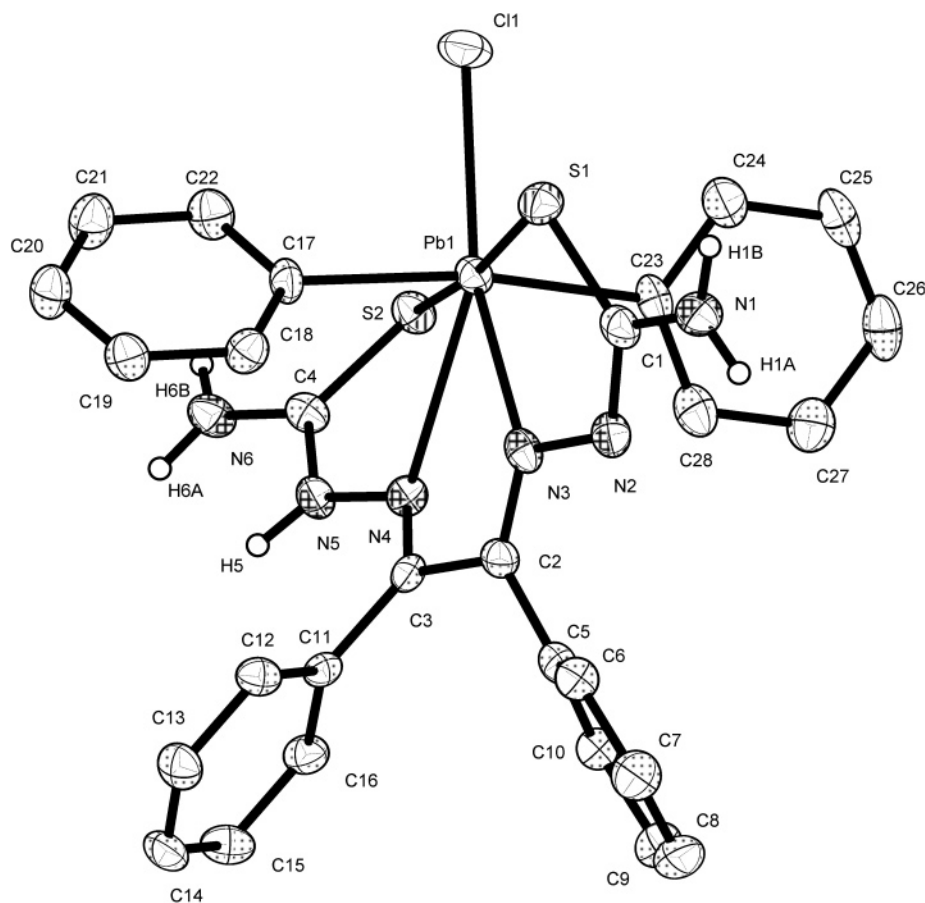


Figure 1. Molecular structure of complex $[\text{PbPh}_2\text{Cl}(\text{L}^1\text{H}_5)] \cdot 3\text{H}_2\text{O}$ (**1**), with thermal ellipsoids shown at 50% probability. Selected bond lengths (\AA) and angles (deg): $\text{Pb}(1)\text{--C}(17)$ 2.190(4), $\text{Pb}(1)\text{--C}(23)$ 2.193(4), $\text{Pb}(1)\text{--N}(3)$ 2.584(4), $\text{Pb}(1)\text{--Cl}(1)$ 2.6645(11), $\text{Pb}(1)\text{--S}(1)$ 2.7056(11), $\text{Pb}(1)\text{--N}(4)$ 2.757(4), $\text{Pb}(1)\text{--S}(2)$ 2.9810(11), $\text{C}(1)\text{--N}(2)$ 1.330(6), $\text{C}(1)\text{--N}(1)$ 1.335(6), $\text{C}(1)\text{--S}(1)$ 1.743(5), $\text{C}(2)\text{--N}(3)$ 1.304(6), $\text{C}(2)\text{--C}(3)$ 1.488(6), $\text{C}(3)\text{--N}(4)$ 1.294(6), $\text{C}(4)\text{--N}(6)$ 1.322(6), $\text{C}(4)\text{--N}(5)$ 1.362(6), $\text{C}(4)\text{--S}(2)$ 1.693(4), $\text{N}(2)\text{--N}(3)$ 1.375(5), $\text{N}(4)\text{--N}(5)$ 1.365(5), $\text{C}(17)\text{--Pb}(1)\text{--C}(23)$ 168.25(17), $\text{C}(17)\text{--Pb}(1)\text{--N}(3)$ 94.40(14), $\text{C}(23)\text{--Pb}(1)\text{--N}(3)$ 83.12(14), $\text{C}(17)\text{--Pb}(1)\text{--Cl}(1)$ 92.16(12), $\text{C}(23)\text{--Pb}(1)\text{--Cl}(1)$ 94.97(13), $\text{N}(3)\text{--Pb}(1)\text{--Cl}(1)$, 154.45(9), $\text{C}(17)\text{--Pb}(1)\text{--S}(1)$ 96.31(12), $\text{C}(23)\text{--Pb}(1)\text{--S}(1)$ 93.49(12), $\text{N}(3)\text{--Pb}(1)\text{--S}(1)$ 68.74(8), $\text{Cl}(1)\text{--Pb}(1)\text{--S}(1)$ 86.01(4), $\text{C}(17)\text{--Pb}(1)\text{--N}(4)$ 75.76(14), $\text{C}(23)\text{--Pb}(1)\text{--N}(4)$ 93.09(14), $\text{N}(3)\text{--Pb}(1)\text{--N}(4)$ 61.13(11), $\text{Cl}(1)\text{--Pb}(1)\text{--N}(4)$, 144.30(8), $\text{S}(1)\text{--Pb}(1)\text{--N}(4)$ 128.12(8), $\text{C}(17)\text{--Pb}(1)\text{--S}(2)$ 87.42(12), $\text{C}(23)\text{--Pb}(1)\text{--S}(2)$ 84.46(4), $\text{S}(1)\text{--Pb}(1)\text{--S}(2)$ 169.90(3), $\text{N}(4)\text{--Pb}(1)\text{--S}(2)$ 61.89(8).

in agreement with the deprotonation of the ligand. The spectrum of complex **6** is very similar to that of complex **5**, so the ligand has also lost the methoxy group and the amine nitrogen atom. The coupling constants corresponding to the organometallic moiety $^3J(^{207}\text{Pb}\text{--}^1\text{H})$ are 159 and 162.1 MHz, respectively. These values are smaller than those for a coordination number of six, suggesting that in solution the coordination number is five or even four.^{11–13} The ^{207}Pb chemical shifts are also coherent with a coordination number smaller than six,³⁹ suggesting that some bonds have been broken in solution.

The changes observed in the ^{13}C NMR spectra of complexes **5** and **6** with respect to the free $\text{L}^2\text{H}_2\text{OCH}_3$ agree with a NS coordination of the ligand; the presence of several signals in the range of the imine carbons in the spectrum of complex **5** suggests two kinds of coordination modes for the ligands. The values of $^2J(^{207}\text{Pb}\text{--}^{13}\text{C})$ are 109.5 and 113.9 MHz, respectively, close to those observed in a coordination number of five. The ^{207}Pb NMR shift for complex **5** was observed at -211 or at -315 ppm in CDCl_3 or DMSO solution, respectively. These values are also coherent with a coordination number smaller than six and with the DMSO coordinated to the lead atom. The ^{207}Pb NMR spectrum of

complex **6** in CDCl_3 shows a signal at -122.5 ppm, which is in the range of a coordination number of four. These NMR data indicate that one of the $\text{Pb}\text{--L}$ bonds must be broken in solution, as happened in the organotin derivatives with this ligand.²³ The signal in the spectrum of complex **7** (-771.6 ppm) is the highest observed in our compounds and agrees with the solvent being coordinated to the lead atom.

^{13}C CP/MAS NMR spectra were also recorded for all the complexes. The shifts observed confirm the N_2S_2 coordination for both open-chain ligands. In addition, the number of signals agrees with the asymmetry proposed in complexes **1** and **3**, in which the ligands has only displaced one chloride ion, or in those in which the ligands also act as bridge through the sulfur atoms, complexes **2** and **4**.

The spectra of all $\text{L}^2\text{H}_2\text{OCH}_3$ derivatives support the loss of a methanol molecule. In all the complexes obtained from the cyclic ligands, the shifts observed in the thioamide carbon confirm that the sulfur atom is bonded to the lead.

Solid-State Structures. Crystallographic data for the structures solved are given in Table 1. The structures of complexes **1** and **3** are, as far as we know, the first examples of organolead(IV) complexes containing a bis(thiosemicarbazone), and they state the importance of the substitution in

the terminal amine group. The structure of **5** is the first complex containing two triazine thione ligands showing linkage isomerism.

The crystal structure of complex **1** is made up of $[\text{PbPh}_2\text{-Cl}(\text{L}^1\text{H}_5)]$ units with three molecules of water held together in the crystal packing by hydrogen bonds. The molecular structure of **1** is shown together with the numbering scheme and selected bond lengths and angles in Figure 1. The coordination sphere of the lead atom is formed by the two sulfur atoms and the two imine nitrogen atoms from the benzil bis(thiosemicarbazone) ligand, one Cl, and two phenyl groups. The geometry around the metal can be described as a distorted pentagonal bipyramid with the phenyl groups being axial, whose C–Pb–C angle, $168.27(17)^\circ$, differs from the ideal 180° , and the lead atom on the equatorial plane defined by S, N, N, S, and Cl. In all the complexes previously published, this ligand can be considered planar,¹⁷ but in this complex is strongly twisted, with one sulfur atom above the least-squares plane and the other under, which could be induced by the presence of chloride and phenyls bonded to the lead atom. The pseudomacrocyclic coordination mode of the ligand affords three five-membered chelate rings. The asymmetric behavior of the thiosemicarbazone branches, due to the presence of the hydrogen atom of a secondary amine in only one thiosemicarbazone moiety, is reflected on the values of the bond distances of the ligand backbone. In addition, two different Pb–S distances are observed. The one corresponding to the neutral branch, $2.9810(11) \text{ \AA}$ is longer than the anionic one, $2.7056(11) \text{ \AA}$, suggesting that the neutral is less basic than the deprotonated one or the presence of an additional electrostatic attraction in the anionic part of the ligand. Similar differences between both arms are observed in the Pb–N bonds; one distance in the neutral one is 0.173 \AA longer than in the anionic one. The C(1)–S(1) distance in the deprotonated thiosemicarbazone is 0.05 \AA larger than in the non-deprotonated one and is consistent with a bond order close to one. This difference is the greatest observed in complexes from L^1H_6 .¹⁸ The C(3)–N(4) and C(2)–N(3) distances show the same differences. These data confirm there is extensive conjugation within the ligand, which is greater in the deprotonated thiosemicarbazone branch. The Pb–Cl distance, $2.6645(11) \text{ \AA}$, is shorter than in other thiosemicarbazones complex with close geometry.¹¹ Remaining bond distances and angles are similar to those found in related complexes and do not deserve further comments. Finally, the molecules are held together in the crystal packing through an extended network of intermolecular hydrogen bonds involving the primary amine groups, S(2) and N(2) atoms, and the oxygen atom from the water molecules (see Figure 2 and Table 2) and through π – π interactions between the phenyl groups.

Figure 3 shows the molecular structure, numbering, and selected bond lengths and angles of the adduct **4**. The compound is a centrosymmetric dimer in which each lead atom is coordinated to two sulfur and two nitrogen atoms of the benzil bis(thiosemicarbazone), two phenyl carbon atoms, and also to one of the sulfur atoms of a second bis(thiosemicarbazone) ligand. The coordination geometry of

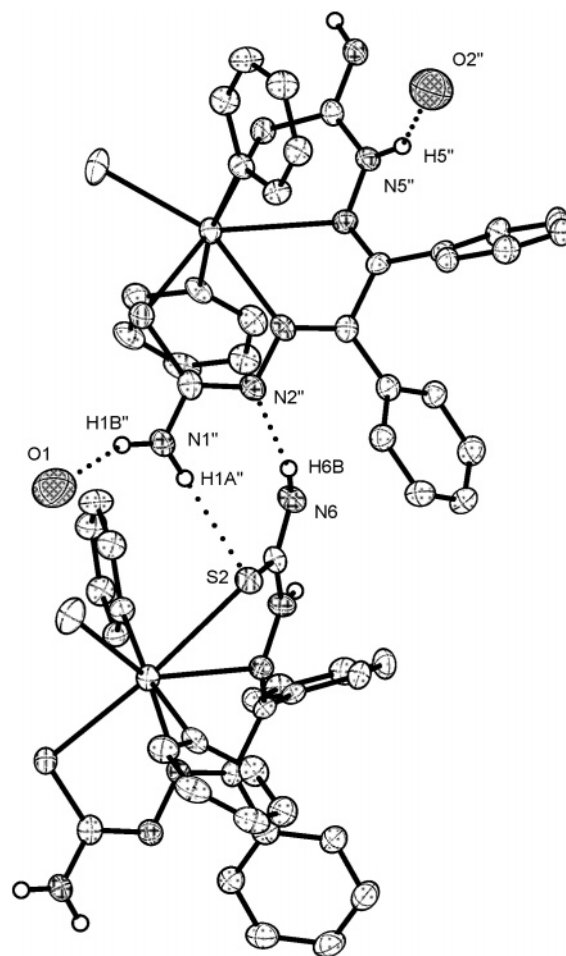


Figure 2. Plot including the hydrogen bonds in complex **1**.

Table 2. Hydrogen Bonds (\AA , deg) in Complex **1**^a

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	\angle (DHA)
N(1)–H(1A)···S(2)#1	0.86	2.52	3.380(4)	173.6
N(1)–H(1B)···O(1)#1	0.86	2.36	3.080(6)	142.0
N(6)–H(6B)···N(2)#2	0.86	2.24	3.073(5)	164.5
N(5)–H(5)···O(2)#3	0.862(19)	2.40(3)	3.110(7)	140(4)

^a Symmetry transformations used to generate equivalent atoms: #1 $-x + 3/2, y - 1/2, z$; #2 $-x + 3/2, y + 1/2, z$; #3 $x + 1/2, y, -z + 1/2$.

the metal may be regarded as a distorted pentagonal bipyramid in which the axial positions are occupied by the phenyl ligands with a deviation from the linearity of the C–Pb–C angle of only 5° . As in complex **1**, the ligand is twisted, although the distortion in this case is much smaller since there is no chloride bonded to the metal. The Pb–S bonds, $2.8040(12)$ and $2.8006(12) \text{ \AA}$, are intermediate between those observed in the thiosemicarbazone and thiosemicarbazone branches in complex **1**. The C(1)–S(1) distance (sulfur bridge) is longer than the corresponding to the monodentate sulfur atom and both are larger than in the free ligand ($1.676(3) \text{ \AA}$).²⁶ The weakening of this bond allows an additional bond with another lead atom to form the dimeric unit. The C–N distances are longer than in $\text{L}^1\text{-Me}_2\text{H}_4$ ²⁶ and similar to that distance observed in the thiosemicarbazone branch in complex **1**. Bond lengths agree with a considerable electronic delocalization through the 4-methyl-3-thiosemicarbazone backbones, which is

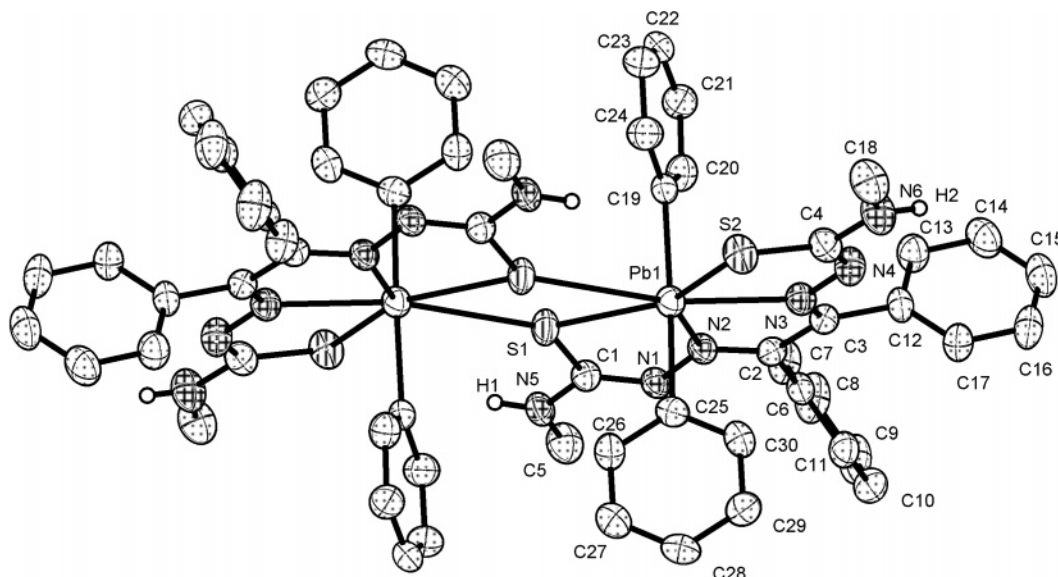


Figure 3. Molecular structure of complex $[\text{PbPh}_2(\text{L}^1\text{Me}_2\text{H}_2)]_2 \cdot 2\text{H}_2\text{O}$ (**4**), with thermal ellipsoids shown at 40% probability. Selected bond lengths (\AA) and angles (deg): Pb(1)–S(1) 2.8046(12), Pb(1)–S(1)#1 3.2577(11), Pb(1)–N(2) 2.443(4), Pb(1)–N(3) 2.429(4), Pb(1)–S(2) 2.8006(12), Pb(1)–C(19) 2.185(5), Pb(1)–C(25) 2.199(5), S(1)–C(1) 1.740(5), C(1)–N(1) 1.323(6), C(1)–N(5) 1.355(6), C(2)–C(3) 1.496(6), C(3)–N(3) 1.309(6), C(4)–N(4) 1.339(6), C(4)–S(2) 1.721(5), C(4)–N(6) 1.354(6), C(5)–N(5) 1.452(7), C(18)–N(6) 1.449(7), N(1)–N(2) 1.375(5), N(3)–N(4) 1.357(5), S(1)–Pb(1)–S(1)# 67.27(4), S(1)–Pb(1)–N(2) 69.31(9), S(1)–Pb(1)–N(2) 136.26(9), S(1)–Pb(1)–N(3) 137.08(9), S(1)#–Pb(1)–N(3) 155.40(9), N(2)–Pb(1)–N(3) 68.34(12), S(1)–Pb(1)–S(2) 151.95(3), S(1)#–Pb(1)–S(2) 84.87(3), N(2)–Pb(1)–S(2) 138.73(9), N(3)–Pb(1)–S(2) 70.58(9), S(1)–Pb(1)–C(19) 87.37(11), S(1)#–Pb(1)–C(19) 88.77(12), N(2)–Pb(1)–C(19) 94.29(15), N(3)–Pb(1)–C(19) 89.11(14), S(2)–Pb(1)–C(19) 88.83(12), S(1)–Pb(1)–C(25) 93.89(12), S(1)#–Pb(1)–C(25) 86.94(12). Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y + 1, -z + 1$.

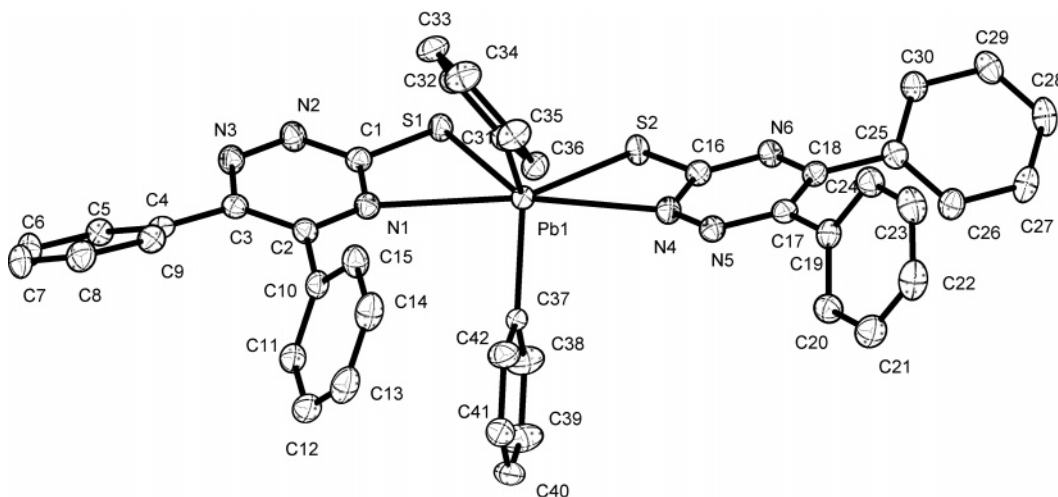


Figure 4. Molecular structure of complex $[\text{PbPh}_2(\text{L}^2)]$ (**5**), with thermal ellipsoids shown at 50% probability. Selected bond lengths (\AA) and angles (deg): Pb(1)–C(37) 2.189(2), Pb(1)–C(31) 2.194(2), Pb(1)–S(1) 2.5763(6), Pb(1)–S(2) 2.5868(6), Pb(1)–N(1) 2.795(2), Pb(1)–N(4) 2.805(2), C(1)–N(2) 1.342(3), C(1)–N(1) 1.348(3), C(1)–S(1) 1.751(3), C(2)–N(1) 1.331(3), C(2)–C(3) 1.412(3), C(3)–N(3) 1.345(3), N(2)–N(3) 1.337(3), N(4)–N(5) 1.337(3), C(37)–Pb(1)–C(31) 120.13(9), C(37)–Pb(1)–S(1) 116.11(6), C(31)–Pb(1)–S(1) 104.01(7), C(37)–Pb(1)–S(2) 110.81(6), C(31)–Pb(1)–S(2) 113.63(6), S(1)–Pb(1)–S(2) 87.447(18), C(37)–Pb(1)–N(1) 84.29(7), C(31)–Pb(1)–N(1) 80.46(8), S(1)–Pb(1)–N(1) 58.85(5), S(2)–Pb(1)–N(1) 146.16(5), C(37)–Pb(1)–N(4) 88.56(7), C(31)–Pb(1)–N(4) 82.74(8), S(1)–Pb(1)–N(4) 143.95(4), S(2)–Pb(1)–N(4) 58.20(5), N(1)–Pb(1)–N(4) 155.20(6).

enhanced upon deprotonation. There is π stacking between the aromatic rings, as well as an O–H \cdots S hydrogen bond between the oxygen atom and one of the sulfur atoms, O(1) \cdots S(2) at 3.302(7) \AA , while the NH group does not appear to participate in this kind of interaction.

The crystal structure of complex **5** consists of discrete molecules of $[\text{PbPh}_2(\text{L}^2)]$. A perspective view of the complex together with the atom labeling scheme and selected bond angles and distances are given in Figure 4. Within the complex, the lead(IV) ion is hexacoordinated in a strongly distorted octahedral arrangement, four of the coordination positions belonging to the NS deprotonated ligands and the

two remaining positions in the octahedral geometry are occupied by two phenyl groups with a C–Pb–C angle of 120.13(9) $^\circ$. This value is intermediate between the ideal value for the cis (90 $^\circ$) and the trans isomer (180 $^\circ$), a similar situation to that found in similar tin complexes (122–155 $^\circ$), which suggests that the geometry of the complex can be described as a distorted trapezoidal bipyramid⁴¹ in which the equatorial plane is formed by the sulfur and nitrogen atoms and the axial position are occupied by the two phenyl groups. Another possibility is to consider the compound as a bicapped

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tetrahedron defined by the carbon and sulfur atoms, with four tetrahedral angles close to the ideal value angles distorted by the influence of the capping atoms.^{42,43}

The four positions occupied by the ligand are through the amine nitrogen atom N(4), the new imine nitrogen N(1), and the sulfur atoms S(1) and S(2). This behavior is a good example of linkage isomerism and it is observed for the first time in 1,2,4-triazine-3-thione ligands. The coordination mode of the ligands gives rise to two four-membered chelate rings. Each triazine, including the sulfur atom, can be considered planar, with maximum deviations of 0.019 and 0.015 Å for N(2) and C(18), respectively. Bond lengths in the complex agree well with an imine–thione form of the ligand, as does the NMR spectroscopy, but with considerable electronic delocalization through the triazine ring, owing to the deprotonation of the ligand. As a consequence of this delocalization, all the C–N bonds have almost the same length (Figure 4). The thione bonds are longer than in the precursor molecule (1.628 Å in L²H₂OCH₃) and are intermediate between the theoretical C–S single and double bonds,⁴⁴ as is also the case with the N–N bonds. Both S–C–N angles are also modified, but they do not reflect the different nitrogen atoms involved in the coordination. The Pb–S distances are very similar and quite shorter than in the open-chain complexes. In contrast, due to the small bite of the triazines, the Pb–N distances are quite long and in the limit range of this kind of bonds.

Conclusions

The reactions were carried out in different conditions, but the best results were obtained using methanol or dried CH₂-

Cl₂ in the presence of basic medium. In all the complexes the ligands act as anions. In the complexes containing the open-chain ligands, these act at least as an N₂S₂ chelate. In complexes **1** and **3**, the lead atom is heptacoordinated with a C₂N₂S₂Cl environment in a monomeric structure. Moreover, complex **4** shows a binuclear structure in which each lead atom has a C₂N₂S₃ environment with the ligand acting as a N₂S₂ chelate and sulfur bridge. The data of complex **2** suggest a binuclear structure with the dideprotonated ligand acting as N₂S₂ chelate and sulfur bridge. The cyclic ligand derivatives are mononuclear complexes with the ligand acting as bidentate NS. Complexes **5–7** show that the ligands are deprotonated with a distorted octahedral geometry around the lead atom. In addition, complex **5** shows linkage isomerism since one of the ligands is bonded through the amine nitrogen, while in the other one, the nitrogen involved in the coordination is the new imine group, behavior observed for the first time in this ligand. In the absence of crystallographic data for complex **6**, its analytical data and spectroscopic characteristics are consistent with a five-coordinate lead atom in a monomeric structure.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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