Synthesis, Characterization and Crystal Structure of Bis(benzoyl-thiobenzoyl-methanato-O,S)diphenyl Lead

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Ambideterminate Ligands, Bis(benzoyl-thiobenzoyl-methanato-O,S)diphenyl Lead. X-Ray

Bis(benzoyl-thiobenzoyl-methanato-O,S)diphenyl lead has been synthesized and characterized by IR and NMR spectra. Its crystal and molecular structure reveals that the lead atom possesses a skew-trapezoidal bipyramidal environment with pairs of the same donor atoms (O and S) in the cis position, and the two phenyl groups settled with a C–Sn–C bond angle of 138.4(2)°. The Pb–O bonds are longer than the Pb–S bonds revealing the ambideterminate nature of this ligand.

Introduction

Among diorganotin bis-chelate R2SnL2 complexes, a large variation has been noted in overall structure [1]. For example one can find the two organo moieties R spanning from cis to trans orientation in an octahedral configuration, and the ligand L may either be monodentate, anisobidentate or bidentate. In contrast to the tin complexes the structure of the only a rather limited number of organolead compounds R2PbL2 has been investigated by X-ray diffraction methods [2]. The only sulfur-ligand compound of this type presently examined is, to our knowledge, diphenylead bis(O,O-dibenzyldithiophosphate) [3]. However, sulfur containing bidentate ligands such as benzoylthiobenzoyl)methane, PhC(S)CH2 C(O)Ph, in reference to main group elements display considerable variance as chelating ligands [4]. In addition, some of the metal complexes undergo intramolecular rearrangement to give an organic sulfide [5, 6]. This has prompted us to synthesize, characterize and examine the crystal and molecular structure of Ph2Pb[PhC(S)CH2(C(O)Ph)] (I) derived from benzoyl(thiobenzoyl)methane.

Experimental

All experimental manipulations and the solvent purification were as described previously [4]. Benzoyl(thiobenzoyl)methane was prepared by the literature procedure [7]. Diphenylead dichloride (Alfa) was recrystallized from ethanol before use. Lead was gravimetrically determined as PbCrO4.

Carbon and hydrogen were analyzed by an elemental analyzer. The IR spectrum was recorded on a Perkin-Elmer 621 model in the range 4000–200 cm-1. 'H and 13C NMR spectra were obtained from a JEOL FX 90Q spectrometer in CDCl3 with SiMe4 as internal reference.

Analysis for Pb2Ph(PhCSCCHOCPh)2

Calcd Pb 24.6 C 60.1 H 3.8%
Found Pb 24.0 C 59.9 H 3.5%

X-ray structure determination

The X-ray structure was determined using a Nicolet R3m four-circle automated diffractometer equipped with a graphite monochromator (Mo–Kα radiation, λ = 0.71069 Å) for data collection at 25 °C and the SHELXTL-PLUS program package for structure solution and refinement. Single crystals of I were grown from hot ethyl acetate solution and mounted in glass capillaries. The
unit cell dimensions were determined from the setting angles of 25 high angle reflections. An empirical absorption correction based on $\psi$-scans was applied (max./min. transmission: 0.843/0.626) besides Lorentz and polarization as well as anomalous extinction corrections. The structure was solved by direct methods. All non hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and included with isotropic temperature factors in the final stages of refinement.

Crystal data:

$C_{47}H_{34}S_{7}O_{2}Pb$, $M_r = 840.0$, $a = 9.936(1)$, $b = 18.846(2)$, $c = 19.371(2)$ Å, $\beta = 97.78(2)^\circ$, $V = 3594(2)$ Å$^3$, $D_{calc} = 1.552$ Mg/m$^3$, $Z = 4$, monoclinic space group $P2_1/c$ (No. 14), $F(000) = 1656$, $\mu = 48.7$ cm$^{-1}$. Crystal size, 0.2 x 0.3 x 0.4 mm, $\omega$-Scans, 2$\theta$-range: 4–46° in $h$, $\pm k$, $\pm l$, scan width: 0.8°, scan speed: 1.8 to 29.3°/min; 2 check reflections were monitored after every 48 intensity measurements; 13036 measured reflections, 6083 of which were unique (and intensity averaged) and 5067 observed with $F > 4\sigma(F)$. Final $R = 0.035$, $R_w = 0.047$; 424 parameters refined; largest residual electron density: 2.09 e/Å$^3$ close to Pb and S(1). Final atomic coordinates are given in Table I [8].

Results and Discussion

$\text{Ph}_2\text{Pb(PhC(S)CHC(O)Ph)}_2$ (1) was prepared from the reaction of diphenyllead dichloride and benzoyl(thiobenzoyl)methane in the presence of aqueous ammonia in ethyl acetate as a yellow crystalline solid according to eq. (1).

$$\text{Ph}_2\text{PbCl}_2 + 2 \text{PhC(S)CHC(O)Ph} + 2 \text{NH}_3 \rightarrow \text{Ph}_2\text{Pb(PhC(S)CHC(O)Ph)}_2 + 2 \text{NH}_4\text{Cl} \quad (1)$$

Its infrared spectrum displays two characteristic absorptions at 1595 and 1560 cm$^{-1}$, due to $\nu$(CO) and $\nu$(C=C) modes, respectively. The position of the former is similar to the corresponding diorganothiotin complexes [4] which have been found to possess approximately a skew-trapezoidal bipyramidal structure with the two organo groups oriented at $\approx 135^\circ$; the ligands chelate with weak Sn–O bonds. $^1$H and $^{13}$C NMR spectra of the lead complex are not of much diagnostic value for structural assignment. The $^1$H NMR spectrum contains a multiplet at $\delta = 6.2$–8.2 ppm due to methine and phenyl protons. The $^{13}$C NMR data comprise in addition to phenyl and methine carbon signals, C(S) at 187.8 and C(O) at 174.3 ppm; the position of the latter is indicative of only weak coordination by the carbonyl oxygen to the lead center. However, the single set of signals for the ligand L suggests the presence of a fairly symmetrical complex or fluxionality associated with weak Pb–O-binding. No definite information as to the true structure of the complex can be derived from these data. Therefore, crystals of 1 were subjected to an X-ray structure analysis.

The result is displayed in Fig. 1, together with a selection of bond lengths and angles in the legend. The two ligands L chelate the lead atom to give a six-coordinate environment. A detailed analysis of the parameters reveals, however, that the polyhedron around the lead atom can be described as an example of a skew-trapezoidal bipyramid with pairs of donor atoms (O and S) in cis positions constituting a trapezoid. The two phenyl groups with a C(1)–Pb–C(7) bond angle of 139.4(2)$^\circ$ are skewed towards a common edge of the trapezoid along the bisector of the tin-oxygen distances. This...
relatively less known structure is, to our knowledge, the first of its kind in lead chemistry. Actually, this atomic arrangement turns out to be almost identical with the coordination core of the dimethyltin complex, Me₂Sn[PhC(S)CHC(O)Ph]₂, demonstrating that structural chemistry of lead closely parallels that of its lighter congener, tin. It also suggests that the geometry of this type can occur with the six-membered chelate ring of the thio-β-diketone ligand which has a larger normalized bite and is not necessarily confined to the four-membered chelate rings exemplified by monothiocarbaminate ligands [9] having a shorter bite.

The planar trapezoid in addition to acute intrachelate angles (average 76.9°) at the tin atom of Me₂SnL₂ does not differ much from the interchelate S(1)–Pb–S(2) angle of 76.3(1)° in 1. Consequently, the O(1)–Pb–O(2) angle (130.01(1)°) is a fairly wide one. The nonbonding S–S contact in 1 is found to be 3.225 Å which is significantly shorter than the van der Waals contact (3.79 Å). The Pb–S bond lengths averages to 2.621 Å (see legend to Fig. 1) corresponding closely to a single bond (calc. from atomic radii: 2.58 Å). However, the Pb–S bond lengths observed in 1 are shorter than the corresponding bond lengths reported for the dithiophosphate complex, Ph₂Pb[(PhCH₂O)₂PS₂]₂ (shortest Pb–S distance: 2.701 Å) [3]. The average Pb–O distance of 2.574 Å in 1 is about 18% longer than expected from the sum of their atomic radii. This is in consonance with the ¹³C NMR data which indicate an anisobidentate nature of the ligand. The Pb–C bond length of average 2.18 Å falls within the distances formerly reported [2, 3]. In addition, the comparatively shorter C–C bond (average 1.355 Å) adjacent to the C–S bond as compared with the C–C distance (average 1.408 Å) adjacent to the C–O group observed in 1 suggests that the negative charge associated with the ligand mainly resides on the sulfur atom of the complex, and this single bonded C–S contribution most strongly to the electronic ground state of the complex. This is a consistent feature in the metal complexes of the thio-β-diketones [10].

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