were determined by a least-squares calculation of 2θ values of 25 reflections with $19° < 2\theta < 22°$. Intensities were collected on a Rigaku AFC-5 four-cycle automated diffractometer by using Mo $K\alpha$ radiation ($\lambda = 0.710\,68$ Å). Detailed conditions for the data collection are summarized in Table I. No absorption correction was applied.

Calculations were carried out with the program system CRYSTAN on a FACOM A-70 computer. The structure was solved by a combination of direct methods (SAPI85) and Fourier techniques. Full-matrix least-squares calculations were used with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were located at idealized positions with isotropic temperature factors, and their parameters were not refined.

Systematic absences of reflections ($h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 4n$) indicated space group $P4_12_12$ or its enantiomorph $P4_32_12$. As least-squares calculations with the latter space group showed better convergence ($R = 0.052_6$ and $R_w = 0.054_1$) than calculations with the former space group ($R = 0.054_3$ and $R_w = 0.056_1$), structure calculations were carried out with $P4_32_12$.

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Registry No. 1, 127355-85-5; 2, 127355-86-6; 3, 127355-87-7; Ru(cod)(cot), 127382-91-6; 3-butenoic acid, 625-38-7.

Supplementary Material Available: Tables S1 and S2 (fractional coordinates and temperature factors of 1) and Table S3 (bond distances and angles) (6 pages); Table S4 (observed and calculated structure factors) (6 pages). Ordering information is given on any current masthead page.

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^{207}Pb CP MAS NMR Study of Hexaorganyldiplumbanes

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Lead-207 CP MAS NMR spectra have been obtained for the series of hexaorganyldiplumbanes Pb_2R_6 (R = phenyl, *o*-tolyl, *m*-xylyl, mesityl, cyclohexyl). These data will be discussed in relation to the respective solution-state ^{207}Pb NMR spectra and to the complementary information available from crystallographic studies. The ^{207}Pb shielding tensor components will be considered both qualitatively and quantitatively. Three triorganyllead halides have also been examined, and chemical shift data are reported for them.

Introduction

For some not so obvious reasons the ^{207}Pb nucleus in organolead compounds has so far attracted very little attention for high-resolution solid-state NMR studies. There are only a few reports on ^{207}Pb CP MAS studies in the literature,[1-6] although solid-state ^{207}Pb NMR spectroscopy can be expected to become an extremely useful analytical tool in the field of organolead chemistry, on the grounds of what is known from solution-state ^{207}Pb NMR studies.[7]

Especially with organolead(IV) compounds with mainly covalent bonds there are no experimental difficulties in obtaining good-quality ^{207}Pb CP MAS spectra. In this light, the hexaorganyldiplumbanes are ideal candidates for a ^{207}Pb CP MAS study: (i) the symmetrically substituted diplumbanes Pb_2R_6 are reasonably stable compounds, (ii) the X-ray crystal structures of $Pb_2(\text{phenyl})_6$[8] and $Pb_2(\text{cyclohexyl})_6$[9] are known, (iii) most of these compounds are soluble enough to obtain solution-state ^{207}Pb NMR data for comparison purposes, and (iv) recently, the scalar coupling constant $^1J(^{207}Pb^{207}Pb)$ in diplumbanes has attracted the attention of NMR spectroscopists.[10]

In this paper we present a series of ^{207}Pb CP MAS spectra of some hexaorganyldiplumbanes, Pb_2R_6 (R = phenyl, cyclohexyl, *o*-tolyl, *m*-xylyl, mesityl), together with the respective solution-state ^{207}Pb NMR data. During the course of this investigation it became highly desirable to have further crystallographic information on $Pb_2(o\text{-tolyl})_6$.

Table I. ^{207}Pb NMR Data for Hexaorganyldiplumbanes and Related Compounds[a]

	$\delta(^{207}Pb)$/ppm	
compd	soln	solid (half-height width/Hz)
$Pb_2(\text{phenyl})_6$ (I)	−79.8	−131.8 (250) +14.5 (140)
$Pb_2(\text{cyclohexyl})_6$ (II)	+80.2	+140.6 (100)
$Pb_2(o\text{-tolyl})_6$ (III)	−88.7	−83.9 (500)
$Pb_2(p\text{-tolyl})_6$[b] (IV)	−77.6	−95 −66
$Pb_2(m\text{-xylyl})_6$ (V)	−91.2	−92.7 (500)
$Pb_2(\text{mesityl})_6$ (VI)	−154.5	−141.3 (500) −154.1 (500)
$Pb(o\text{-tolyl})_4$	−166.3[d]	−159.2 (250)
$(\text{cyclohexyl})_3PbCl$	+381.6[d]	+321 (500)
$(\text{cyclohexyl})_3PbBr$	+409[d]	*c*
$(\text{mesityl})_3PbI$	−356.8[d]	−350 ± 2 (1600)

[a] Conditions are given in the Experimental Section. $\delta(^{207}Pb)$ for the solid state is accurate to ±0.5 ppm, unless stated otherwise. [b] Data from ref 1. [c] No ^{207}Pb CP MAS spectrum obtained; the failure is possibly due to excessive line broadening as a consequence of residual (^{207}Pb, $^{79/81}$Br) dipolar interactions in the solid state and/or due to $^{79/81}$Br relaxation effects on the cross-polarization experiment. [d] Saturated $CDCl_3$ solution at room temperature.

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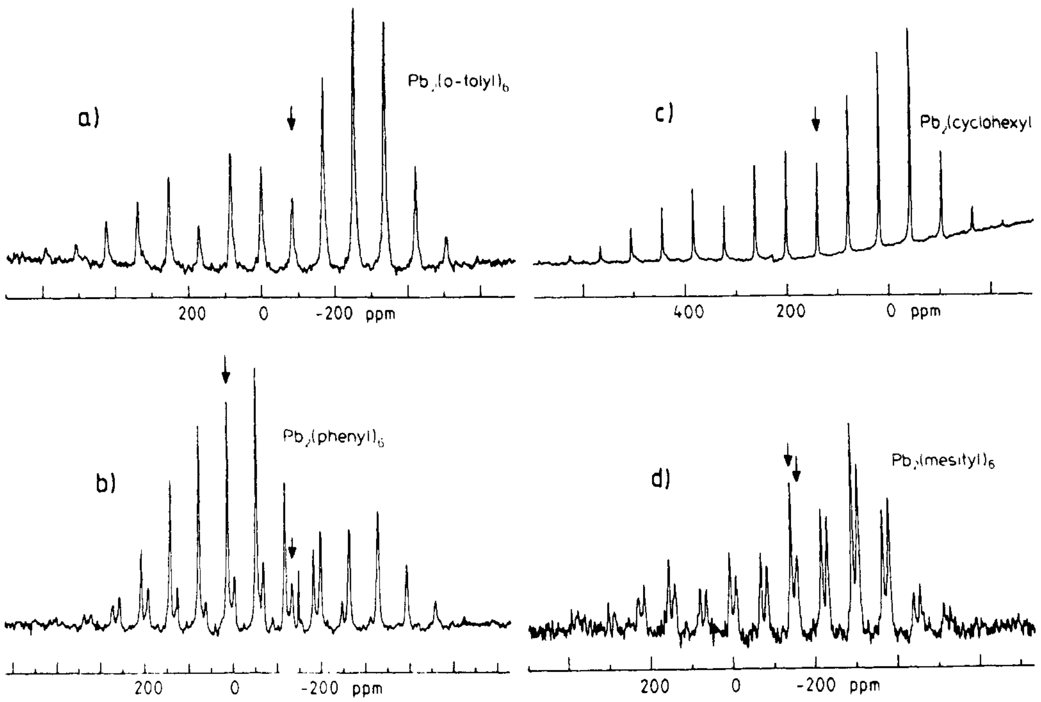

Figure 1. ^{207}Pb CP MAS NMR spectra of some hexaorganyldiplumbanes, Pb_2R_6, with R = *o*-tolyl (a), phenyl (b), cyclohexyl (c), and mesityl (d). Centerbands are indicated by arrows. The experimental conditions were as follows: (a) 6600 transients, 5-s recycle delay, MAS rate 3.5 kHz; (b) 1212 transients, 20-s recycle delay, MAS rate 2.7 kHz; (c) 3088 transients, 5-s recycle delay, MAS rate 2.6 kHz; (d) 1064 transients, 10-s recycle delay, MAS rate 3.5 kHz.

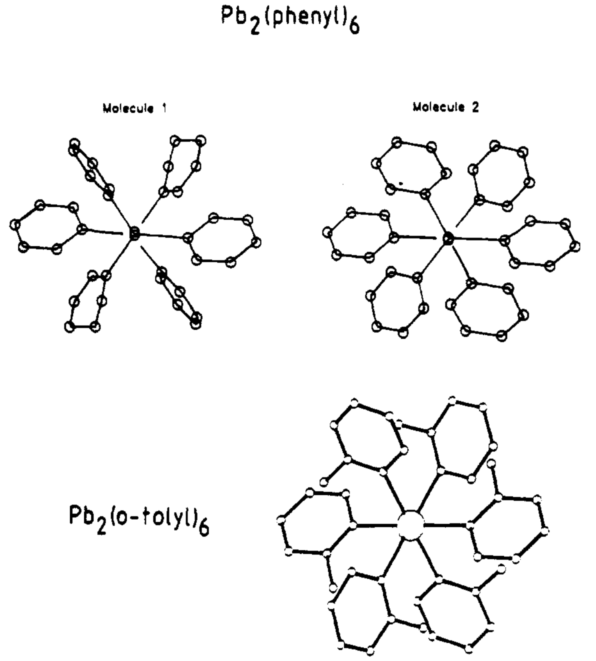

Figure 2. Comparison of the molecular conformations in I, $Pb_2(phenyl)_6$, and III, $Pb_2(o\text{-tolyl})_6$, with the view along the Pb–Pb bonds.

The single-crystal X-ray structure for this compound has been obtained and will be discussed in comparison with the NMR data and with the known X-ray crystal structure of $Pb_2(phenyl)_6$. CP MAS data on hexa-*p*-tolyldilead have

Table II. Shielding Tensor Data for Hexaorganyldiplumbanes[a]

compd	tensor components[b]/ppm σ_{11}	σ_{22}	σ_{33}	anisotropy δ_A/ppm	asymmetry η	σ_{iso}/ppm
$Pb_2(phenyl)_6$ (I)	+219	+2	-265	-251	0.86	-14.5
$Pb_2(phenyl)_6$ (I)	+467	+291	-363	-495	0.35	+131.8
$Pb_2(cyclohexyl)_6$ (II)	+155	+10	-588	-447	0.32	-140.6
$Pb_2(o\text{-tolyl})_6$ (III)	+459	+329	-537	-621	0.21	+83.9
$Pb_2(mesityl)_6$ (VI)	+465	+280	-321	-462	0.40	+141.3
$Pb_2(mesityl)_6$ (VI)	+488	+318	-343	-497	0.34	+154.1

[a] Due to insufficient signal-to-noise ratio and to base line distortions the asymmetry parameters η are accurate only to ±0.05. For R = *p*-tolyl, *m*-xylyl the quality of the spectra are insufficient for a meaningful simulation of the spinning-sideband patterns. [b] From Haeberlen's notation, where $|\sigma_{33} - \sigma_{iso}| \geq |\sigma_{11} - \sigma_{iso}| \geq |\sigma_{22} - \sigma_{iso}|$, $\delta_A = \sigma_{33} - \sigma_{iso}$, and $\eta = (\sigma_{22} - \sigma)/\delta_A$.

Table III. Bond Distances, Bond Angles, and Torsional Angles in III, $Pb_2(o\text{-tolyl})_6$

Bond Distance/pm			
Pb(1)-Pb(1')	289.5 (2)	Pb(1)-C(8)	224.9 (7)
Pb(1)-C(1)	224.2 (5)	Pb(1)-C(15)	224.5 (7)
Bond Angle/deg			
Pb(1')-Pb(1)-C(1)	113.2 (2)	C1)-Pb(1)-C(8)	105.9 (2)
Pb(1')-Pb(1)-C(8)	112.1 (2)	C(1)-Pb(1)-C(15)	105.0 (2)
Pb(1')-Pb(1)-C(15)	113.7 (1)	C(8)-Pb(1)-C(15)	106.2 (3)
Torsional Angle/deg			
C(1)-Pb(1)-Pb(1')-C(8)	-60.2		
C(8)-Pb(1)-Pb(1')-C(1')	60.2		
C(1)-Pb(1)-Pb(1')-C(15')	60.3		
C(15)-Pb(1)-Pb(1')-(1')	-60.3		
C(8)-Pb(1)-Pb(1')-C(15')	-59.5		
C(15)-Pb(1)-Pb(1')-C(8')	59.5		
C(2)-C(1)-Pb(1)-Pb(1')	54.5 (6)		
C(9)-C(8)-Pb(1)-Pb(1')	56.0 (4)		
C(16)-C(15)-Pb(1)-Pb(1')	51.6 (7)		

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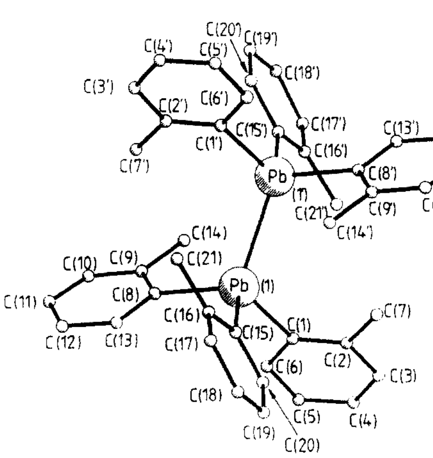

Figure 3. Illustration of the twisting of the *o*-methyl groups in III, $Pb_2(o\text{-tolyl})_6$.

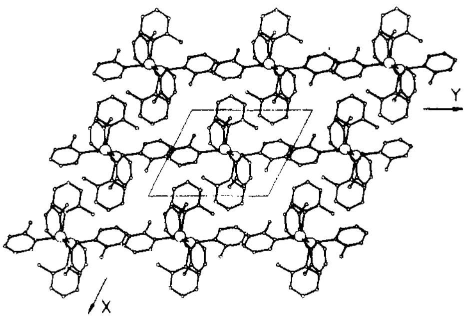

Figure 4. Projection of the structure of $Pb_2(o\text{-tolyl})_6$ onto the *x,y* plane.

been presented earlier.[1]

Results and Discussion

The relevant ^{207}Pb NMR data for Pb_2R_6 (I–VI) are given in Table I, together with some results for related compounds. Table II lists some shielding anisotropy data. The X-ray crystallographic results for $Pb_2(o\text{-tolyl})_6$ (III) are given in Table III. Figure 1 shows the ^{207}Pb CP MAS spectra of compounds I, II, III, and VI. A comparison of the moecular conformations for I and III is depicted in Figure 2. Finally, Figures 3 and 4 further illustrate the X-ray crystal structure of compound III.

The following points are evident from these data.

(i) The chemical shift differences $\Delta\delta(^{207}Pb)$ between the solid state and solution have to be considered as moderate and involve both positive and negative changes. In particular, no significantly higher shielding in the solid state is observed.

(ii) For the compounds II, III, and V (R = cyclohexyl, *o*-tolyl, *m*-xylyl) a single centerband is observed in the ^{207}Pb CP MAS spectra, while compounds, I, IV, and VI (R = phenyl, *p*-tolyl, mesityl) display two centerbands in 1:1 intensity ratios.

(iii) No satellites due to $^1J(^{207}Pb^{207}Pb)$ are observed for compounds I, IV, and VI.

(iv) The spinning-sideband patterns for Pb_2R_6 are typical for axially symmetric or nearly axially symmetric shielding tensors.

(v) The X-ray crystal structure of $Pb_2(o\text{-tolyl})_6$ (III) shows one centrosymmetric molecule per unit cell.

These findings deserve some further comment.

At first glance it may seem surprising that shift differences between the solid and the solution state of up to 60 ppm (II) and 85 ppm (I) are considered as moderate. One must however, bear in mind that the overall ^{207}Pb chemical shift range spans approximately 15 000 ppm. Any inter- or intramolecular association in the solid state would lead to massive ^{207}Pb low-frequency shifts in the solid state, certainly on the order of several hundred ppm. Even in the case of ^{119}Sn an increase in coordination number from 4 to 5 on going from solution to the solid state corresponds to a low-frequency ^{119}Sn shift of approximately 220 ppm.[11] Therefore, all the chemical shift differences $\Delta\delta(^{207}Pb)$ observed for the hexaorganyldiplumbanes I–VI have to be related to purely conformational or packing effects. This is also neatly illustrated by the ^{207}Pb CP MAS spectrum of I, $Pb_2(phenyl)_6$ (see Figure 1), which shows two centerbands at −131.8 and +14.5 ppm, respectively. Inspection of the X-ray crystal structure for this compound reveals two centrosymmetric, independent molecules per unit cell, in fairly different conformations (see Figure 2). The lack of significant changes in chemical shift between the solution and solid states is particularly notable for $(cyclohexyl)_3PbCl$ and $(mesityl)_3PbI$, since these halides might be supposed to be susceptible to expansion of coordination. However, the ^{119}Sn shifts of trialkyltin halides also show[11] little change from the solution of the solid state (in contrast to the case for trialkyltin fluorides). No splittings arising from residual dipolar interactions between ^{207}Pb and halide nuclei were observed in our ^{207}Pb spectra (in contrast to the corresponding ^{119}Sn cases), but it is possible that the failure to obtain a spectrum of solid $(cyclohexyl)_3PbBr$ arose because of excessive line broadening due to the dipolar effect or because of $^{79/81}Br$ relaxation effects on the ^1H–^{207}Pb CP behavior.

For the compounds III, V, and VI (R = *o*-tolyl, *m*-xylyl, mesityl) the very small $\Delta\delta(^{207}Pb)$ values clearly indicate that the rigid conformation in the solid state must be almost identical with the average (on the NMR time scale) conformation in noncoordinating solvents such as $CDCl_3$, whereas the conformation probably changes more significantly with phase for the remaining compounds. For I, $Pb_2(phenyl)_6$, the average of the solid-state ^{207}Pb chemical shifts (−85.6 ppm) is also quite similar to the chemical shift in solution. This indicates a conformational equilibrium in solution that might be described by the two rigid solid-state conformations as the extremes. The same is true for IV, $Pb_2(p\text{-tolyl})_6$. A more substantial change in conformation must be postulated for II, $Pb_2(cyclohexyl)_6$. This finding is not surprising, taking the steric requirements of the bulky cyclohexyl ligands into account. Inspection of Figure 4 also stresses the fact that the observed chemical shift differences are solely caused by conformational and/or packing effects. It is clearly to be seen that there is no expansion of coordination for III. The remaining compounds in Table I fall into a similar category. The modest differences in the solution- and solid-state ^{207}Pb chemical shifts again indicate the absence of coordination changes in the solid state.

The next point concerns the varying number of centerbands (one or two) in the ^{207}Pb CP MAS spectra of I–VI and their relative splittings. In order to show just one centerband, hexaorganyldiplumbanes must be in symmetric conformations (center or plane or axis of symmetry in the middle of the Pb–Pb bond), and their crystal symmetry is restricted to either one molecule per unit cell or, if more than one, then symmetry-related molecules in the unit cell. In other words, the crystallographic asymmetric unit must be half a molecule. We find one centerband for II (R = cyclohexyl), III (R = *o*-tolyl), and V (R = *m*-xylyl)

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within the limitations set by the line widths. This finding is corroborated by the known X-ray crystal structures of II[9] and III (see below). For III there is only one centrosymmetric molecule per unit cell, while for II three symmetry-related (C_3 axis) molecules per unit cell are found.

No crystallographic information on V is available, but a comparison of the data in Table I suggests a very similar situation as for III, Pb_2(*o*-tolyl)$_6$, i.e. a centrosymmetric molecule, and probably a space group similar to that for III.

A discussion of those cases where two centerbands are observed in the ^{207}Pb CP MAS spectra is bound to be somewhat more speculative, as it is only for I, Pb_2(phenyl)$_6$, that the X-ray crystal structure is known.[8] We find two centerbands in a 1:1 intensity ratio (from integration over the respective spinning-sideband manifolds) in the ^{207}Pb CP MAS spectra of I (R = phenyl) and VI (R = mesityl), as well as in IV (R = p-tolyl).[1] For Pb_2(phenyl)$_6$ two independent molecules per unit cell are found in the X-ray crystal structure, so it is straightforward to explain the two resonances in the ^{207}Pb CP MAS spectrum in terms of these two different (but each centrosymmetric) molecules. By comparing both the X-ray crystal strutures and the ^{207}Pb CP MAS spectra for Pb_2(phenyl)$_6$ and for Pb_2(*o*-tolyl)$_6$, it is even possible to assign the two resonances in the ^{207}Pb CP MAS spectrum of I to the respective molecules, as follows.

As is shown in Figure 2, the conformation of molecule 2 in I is very similar to the conformation found for Pb_2(*o*-tolyl)$_6$ (III), while molecule 1 in compound I shows a distinctly different conformation. A similar picture emerges from the ^{207}Pb CP MAS spectra of these two compounds (see Figure 1): one of the two spinning-sideband manifolds for compound I is very similar to what is found for compound III, while for the second resonance a quite different envelope of the sideband pattern (and a moderately different isotropic chemical shift) is observed. From this comparison the resonance at −131.8 ppm has to be assigned to molecule 2 in compound I, while the resonance at +14.5 ppm stems from molecule 1. This assignment is further corroborated by the analysis of the principal components of the shielding tensor.

Table II lists the shielding tensor components for those cases where the quality of the spectra was sufficient for a meaningful spinning-sideband pattern analysis. These data confirm what the qualitative inspection of the spectra reveals (see Figure 1). The asymmetries are, with one exception, in the order of 0.3 (i.e. they indicate shielding tensors that are close to axial symmetry). All anisotropies δ_A, again with one exception, are on the order of 500 ppm, which further confirms that within this series of compounds merely subtle conformational effects are responsible for the observed effects. The tensor components for the two different sites in VI, Pb_2(mesityl)$_6$, are almost identical within the limits of accuracy of the data. For I, Pb_2(phenyl)$_6$, we find quite different tensor data for the two different molecules. The data for the resonance at −131.8 ppm are similar to those for most of the other compounds, while the +14.5 ppm resonance displays a highly asymmetric shielding tensor. This supports the assignment of the two resonances to the two different molecules in the crystal structure. Furthermore, the analysis of the tensorial components indicates that a conformation similar to the conformation in Pb_2(*o*-tolyl)$_6$ is characteristic for most compounds Pb_2R_6 in the solid state.

It remains to be explained what causes the two centerbands in the ^{207}Pb CP MAS spectra of IV, Pb_2(*p*-tolyl)$_6$, and VI, Pb_2(mesityl)$_6$. Figure 3 in ref 1 displays a picture very similar, in terms of spinning-side band patterns, to what we find here for Pb_2(phenyl)$_6$ This makes it reasonable to assume that also for Pb_2(*p*-tolyl)$_6$ there should be two independent centrosymmetric molecules per unit cell. However, the crystallographic splitting for IV (29 ppm) is much smaller than for I (146 ppm), and for the time being we cannot exclude with certainty a second possible explanation. It could also be that Pb_2(*p*-tolyl)$_6$ adopts a conformation in the solid state which renders the two lead atoms per molecule inequivalent. In that case, of course, there could be only one moelcule in the crystallographic asymmetric unit. For compound VI, Pb_2(mesityl)$_6$, we encounter a slightly different situation. In fact, the crystallographic splitting for VI (13 ppm) is small, and Figure 1 shows the two spinning-sideband envelopes to be almost identical. We interpret this by assuming that for Pb_2(mesityl)$_6$ the splitting is due to an intramolecular inequivalence of the two Pb(mesityl)$_3$ moieties, rather than due to a crystallographic inequivalence. This interpretation is supported by an earlier finding,[5] where the occurrence of two centerbands in the ^{207}Pb CP MAS spectrum of $(Ph_3Pb)_2S$ could be clearly ascribed to *intra*molecular inequivalence. For $(Ph_3Pb)_2S$ the splitting is also fairly small, and the envelopes of the two spinning-sideband manifolds are very similar. If we postulate two different Pb(mesityl)$_3$ moieties per molecule for VI, the next question to be asked is as follows: why do we not observe satellites due to $^1J(^{207}Pb^{207}Pb)$? In fact, for $(Ph_3Pb)_2S$[5] satellites due to $^2J(^{207}Pb^{207}Pb)$ are seen. The absence of ^{207}Pb satellites in the ^{207}Pb CP MAS spectrum of VI is satisfactorily explained by the results of a solution-state ^{207}Pb NMR study of (phenyl)$_{6-n}$(anisyl)$_n$Pb$_2$ by Granger et al.[10] In this study Granger et al. calculate $^1J(^{207}Pb^{207}Pb)$ for Pb_2(phenyl)$_6$(±407 Hz) and Pb_2(anisyl)$_6$ (±706 Hz). That $^1J(^{207}Pb^{207}Pb)$ can be either positive or negative is not surprising for such heavy nuclei, and it led us to expect a possibly very small value of $|^1J(^{207}Pb^{207}Pb)|$ for Pb_2(mesityl)$_6$. Actually, with a half-height width of 500 Hz for VI, this coupling constant would have to be fairly large in order to be detectable from the ^{207}Pb CP MAS spectrum. In that case we would have to expect an AB pattern for the ^{207}Pb satellites, which again would be difficult to detect, especially in the presence of extensive spinning sidebands. Of course, we cannot exclude the possibility that Pb_2(mesityl)$_6$ has two different molecules with very similar conformations. So far, however, this series of compounds has shown either one molecule in the asymmetric unit (e.g. R = *o*-tolyl, cyclohexyl), or two clearly different conformers in the asymmetric unit (e.g. R = phenyl). The only chance to prove our interpretation could come from the determination of the single-crystal X-ray structure of VI. This, however, will be severely hampered by the limited solubility of VI, which makes it difficult to obtain suitable single crystals.

Experimental Section

All the hexaorganyldiplumbanes and triorganyllead halides were obtained by known methods. The symmetrically substituted hexaaryldiplumbanes were synthesized from (aryl)$_3$PbMgBr via the reaction with (1) $PbCl_2$ and (2) 1,2-dibromoethane in THF.[12] For the preparation of Pb_2(mesityl)$_6$ this method had to be slightly modified: to a Grignard solution, made from 0.3 mol (59.7 g) of mesityl bromide, were added 0.1 mol (27.8 g) of $PbCl_2$ and then 0.15 mol (28.2 g) of 1,2-dibromoethane at −5 °C under argon. The mixture was stirred for 2 h and then hydrolyzed with ice/acetic

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[12] Willemsens, L. C. *Investigations in the Field of Organolead Chemistry*; Schotanus en Jens: Utrecht, The Netherlands, 1965.

acid. The precipitate was filtered off. For further purification the product was boiled in EtOH (in order to remove the side product $(\text{mesityl})_3\text{PbBr}$), and it was finally reprecipitated from $\text{CHCl}_3/\text{MeOH}$. An orange powder was obtained in 50% yield; mp 250 °C. Anal. Found (calcd): C, 57.4 (57.6); H, 5.9 (5.8); Pb, 36.7 (36.7). C and H analyses were obtained from Mikroanalytisches Labor, Institut für Organische Chemie, Universität Mainz.

Solution-state ^{207}Pb NMR spectra were obtained by using Bruker WP 80 and AC 250 spectrometers, both equipped with multinuclear probes. Concentrations and solvents were as follows: $\text{Pb}_2(\text{phenyl})_6$, 50 mg/mL ($\text{CDCl}_3$), room temperature; $\text{Pb}_2(\text{cyclohexyl})_6$, 200 mg/mL ($\text{C}_6\text{D}_6$), room temperature; $\text{Pb}_2(o\text{-tolyl})_6$, 20 mg/mL ($\text{CDCl}_3$), room temperature; $\text{Pb}_2(m\text{-xylyl})_6$, saturated ($\text{CDCl}_3$), room temperature; $\text{Pb}_2(\text{mesityl})_6$, 5 mg/mL (toluene/$\text{CDCl}_3$), 60 °C. The 41.9-MHz ^{207}Pb CP MAS spectra were run on a Bruker CXP 200 spectrometer, using a multinuclear double-bearing probe and 7 mm o.d. ZrO_2 rotors. Spinning rates were between 2.5 and 3.5 kHz. In order to assign centerbands, all CP MAS spectra were recorded at two different spinning rates. The spectrometer setup procedure, i.e. the optimization of the Hartmann–Hahn matching condition for ^{207}Pb, has been described elsewhere.[2] The proton 90° pulse length was set to 5 μs, and the contact time was 5 ms in all cases. Between 1000 and 8000 transients had to be accumulated, with use of recycle delays of 5–20 s.

All ^{207}Pb chemical shifts are given with respect to external PbMe_4, the high-frequency-positive sign convention being used throughout. For the ^{207}Pb CP MAS spectra, $\text{Pb}(p\text{-tolyl})_4$ was used as the tuning/matching sample and as a secondary external reference (−148.8 ppm). Simulation of the spinning-sideband patterns followed the method by Maricq and Waugh,[14] with use of a program written by L. H. Merwin.

The X-ray crystal structure of $\text{Pb}_2(o\text{-tolyl})_6$ was obtained on an Enraf-Nonius CAD4 diffractometer, and the structural data were calculated by using the SHELX-76 program.[13] To collect the diffraction data, a rhomboid single crystal (0.2 × 0.14 × 0.2 mm) was sealed in a glass capillary, monochromatic Mo radiation was used, and 4330 independent reflexes were collected. The position of the lead atoms was obtained from a Patterson synthesis, whereas the carbon atoms were localized by Fourier synthesis. Localization of the hydrogen atoms was not possible ($R = 0.036$).

Crystal data: triclinic, $P1$; $a = 9.356$ (1) Å; $b = 10.744$ (2) Å; $c = 10.99$ (5) Å; $V = 906$ Å^3; molecular weight for $\text{C}_{42}\text{H}_{42}\text{Pb}_2$ 961.20; density 1.78 g/cm^3 from X-ray 1.72 g/cm^3 in Toulet's solution.

Conclusions

The ^{207}Pb CP MAS NMR spectra of a series of closely related hexaorganyldiplumbanes demonstrate the great potential of heavy-metal spin $^1/_2$ nuclei in investigating rather subtle conformational effects in solids. Crystallographically inequivalent sites are easily detected. In addition, this set of data also highlights the mutually useful relationship between complementary information from spectroscopic and crystallographic studies. In fact, the combined use of both methods allows the assignment of ^{207}Pb resonances to specific conformers in the solid state. This assignment is greatly assisted by the substantial chemical shift anisotropy of heavy-metal nuclei such as ^{207}Pb.

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Registry No. I, 3124-01-4; II, 6713-82-2; III, 14908-73-7; V, 127445-43-6; VI, 127421-76-5; $\text{Pb}(o\text{-tolyl})_4$, 67759-29-9; $(\text{cyclohexyl})_3\text{PbCl}$, 117591-21-6; $(\text{cyclohexyl})_3\text{PbBr}$, 104026-66-6; $(\text{mesityl})_3\text{PbI}$, 127421-77-6; PbCl_2, 7758-95-4; mesityl bromide, 576-83-0.

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