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Redetermination of the Zigzag Modification of Plumbocene at 173 K

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Introduction

Group 14 metallocenes in general, and plumbocenes (Cp'_2-Pb) in particular, display an intriguing range of geometries that are not always easily rationalized on energetic grounds.[1] For example, a bent monomer is observed for gaseous plumbocene,[2] although Panattoni found a zigzag polymeric structure in Cp_2-Pb crystals grown by sublimation.[3] Paver, Wright, and co-workers recently reported two additional structural modifications of plumbocene in crystals obtained from toluene solution at 5 °C.[4] One of these is a solvent-free hexameric aggregate, $(Cp_2Pb)_6$, while the other is a toluene-solvated polymeric chain with a sinusoid-like curvature, $(Cp_2Pb{\cdot}C_7H_8)_\infty$ (Figure 1).

Our efforts to make detailed comparisons between these recently identified modifications and the original zigzag form were hampered by the poor quality of the latter's structure determination. It was based on two-dimensional room temperature X-ray data, and a space group ambiguity was present. The final metrical parameters were relatively poor; e.g., C−C bond lengths in the cyclopentadienyl rings varied from 1.22 to 1.54 Å, and the rings were not completely flat (torsion angles ranged up to 9°). For these reasons, we decided to redetermine the structure of plumbocene at low temperature. As this project was initiated before the appearance of Paver and Wright's work, we did not suspect that crystals grown from solution might yield results different from those obtained by sublimation. In fact, we found that crystals grown from a toluene/THF mixture at 27 °C contain the originally reported zigzag morphology.

Experimental Section

X-ray Crystallography of Cp_2Pb. Plumbocene was synthesized according to a literature procedure.[5] A sample was dissolved in THF and then layered with an approximately equal volume of toluene. X-ray-quality crystals were grown from this solvent arrangement over several days at 27 °C. A suitable crystal was located and mounted on a Siemens SMART system for data collection at 173(2) K. Solution and refinement of the structure were accomplished with the SHELXTL-V5.0 set of programs. Relevant crystal and data collection parameters for the present study are given in Table 1.

Table 1. Crystal Data and Summary of X-ray Data Collection

empirical formula	$C_{10}H_{10}Pb$
fw	337.37
cryst color, habit	yellow, plate
cryst dimens	0.13 × 0.10 × 0.04 mm
space group	*Pnma*
	$a = 16.2938(4)$ Å, $\alpha = 90°$
	$b = 9.5386(1)$ Å, $\beta = 90°$
	$c = 5.8963(1)$ Å, $\gamma = 90°$
volume	916.40(3) Å^3
Z	4
density (calcd)	2.445 Mg/m^3
absorption coefficient	18.342 mm^{-1}
F(000)	608
radiation type (wavelength)	Mo Kα (0.710 73 Å)
temperature	173(2) K
R indices ($I > 2s(I) = 792$)[a]	$R_1 = 0.0341$, w$R_2 = 0.0752$
R indices (all data)[a]	$R_1 = 0.0405$, w$R_2 = 0.0869$
goodness of fit on F^2	1.111

[a] Weighting scheme: $w = [\sigma^2(F_o^2) + (AP)^2 + (BP)]^{-1}$, where $P = (F_o^2 + 2F_c^2))/3$ $A = 0.0127$, and $B = 19.00$.

An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames are oriented such that orthogonal wedges of reciprocal space were surveyed; this produced orientation matrices determined from 55 reflections. Final cell constants were calculated from a set of 3318 strong reflections from the actual data collection.

The space group *Pnma* was determined from systematic absences and intensity statistics. A successful direct-methods solution was calculated that provided most of the non-hydrogen atoms from the electron difference map. Several full-matrix least-squares/difference Fourier cycles were performed that located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Comparative bond distances and angles are listed in Table 2.

$Pna2_1$ and *Pnma* are the only two choices for the space group, and both were explored for the correct solution. The initial statistics indicated a mean $|E * E - 1| = 0.844$, which is median between centrosymmetric and noncentrosymmetric. The solution in $Pna2_1$ was unacceptable, as nearly all anisotropic carbon atoms became nonpositive definite as the refinement converged. The refinement gave indications that the structure was actually centrosymmetric with the Flack $x = 0.50$.[6] The *Pnma* solution required the lead atoms to reside on a mirror plane. The μ-cyclopentadienyl group is bisected by this mirror. C(1) appears to librate through the mirror plane in tandem with the other two unique carbons (C(2), C(3)). These were refined with SHELXTL FLAT, SAME, and DELU restraints which are appropriate for high-symmetry rigid groups like cyclopentadienyl. Solution in the space group *Pnma* also mandates an inversion center, and the μ-cyclopentadienyl group is found on either side of it at half-occupancy. Both rings that constitute the disorder model were refined with the same restraints. Altogether, 53 restraints were applied to the model, and all atoms were positive definite.

The space group *Pnma* could be wrong only if the mirror symmetry were to be broken in some fashion. This might happen if the μ-cyclopentadienyl group preferred one side of

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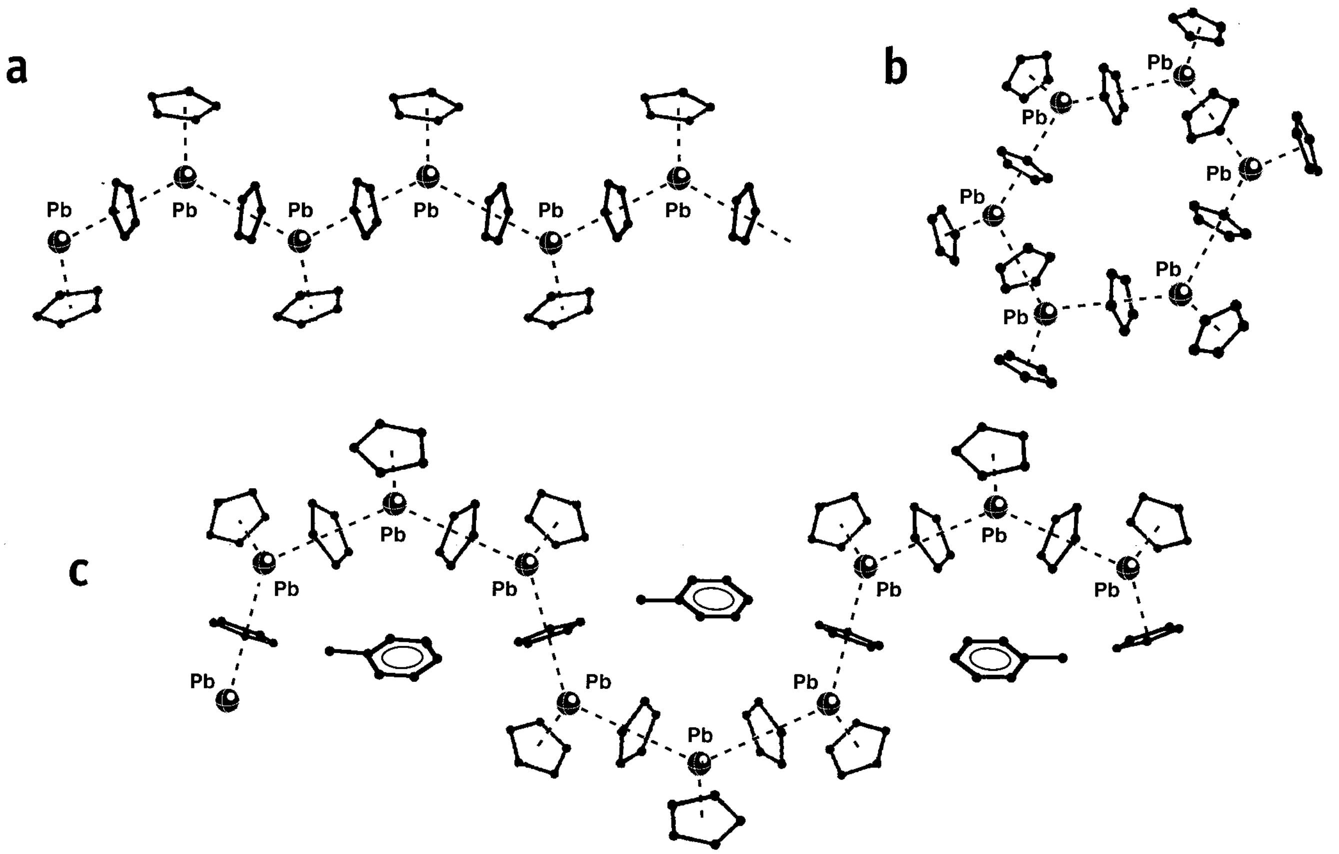

Figure 1. Solid state modifications of plumbocene: a, zigzag form from sublimed crystals; b, solvent-free hexanuclear form from toluene-grown crystals; c, sinusoidal solvate from toluene-grown crystals.

Table 2. Solid State Structural Data for Plumbocene

	zigzag		sinusoidal	hexameric
aggregation	$(Cp_2Pb)_\infty$	$(Cp_2Pb)_\infty$	$(Cp_2Pb\cdot C_7H_8)_\infty$	$(Cp_2Pb)_6$
crystal source	sublimation	toluene/THF	toluene	toluene
crystal system	orthorhombic	orthorhombic	orthorhombic	hexagonal
space group	$Pna2_1$	*Pnma*	*Pnma*	*P6cc*
a, Å	16.37(4)	16.2938(4)	16.421(3)	18.058(2)
b, Å	6.02(3)	9.5386(1)	24.375(5)	
c, Å	9.61(3)	5.8963(1)	8.234(2)	10.219(2)
Pb−C (terminal Cp) (av, range), Å	2.762, 2.589−2.832	2.736(8), 2.718(10)−2.75(2)	2.76(14), 2.73(7)−2.79(5)	2.72(2), 2.64(1)−2.79(1)
Pb−C (bridging ring) (av, range), Å	3.059, 2.973−3.210	2.96(3), 2.94(4)−3.00(2)	3.00(27), 2.93(7)−3.11(7)	2.69−2.90
Pb−centroid (terminal Cp), Å	2.50	2.47	2.50	2.44
Pb−centroid (bridging ring), Å	2.82, 2.83	2.72, 2.89	2.75	2.53
Pb···Pb¢, Å	5.64	5.56	5.50	5.56
ref	3	this work	4	4

the mirror over the other as it wags back and forth. The initial solution in $Pna2_1$ found this group rotated slightly off the position where the mirror would be in *Pnma*. Since no acceptable result could be found in $Pna2_1$, no statistical method (e.g., Hamilton's test[7]) can be used to select the best model.

Results and Discussion

Low-Temperature Structure of Cp_2Pb. Crystals of Cp_2Pb used in this study were obtained from toluene/THF at 27 °C. Nevertheless, the structure determined at 173 K was neither the discrete hexamer nor the sinusoidal toluene solvate,[4] both of which were previously generated from solution-grown crystals, but rather the zigzag polymeric form observed by Panattoni from sublimed crystals (Figure 2).[3] It now seems clear that the critical determinant of the solid state morphology is not the phase from which the sample is obtained but rather the composition and temperature of the solvent. The fact that *three* different structural modifications of plumbocene can be obtained from solution points to an unusually flexible bonding arrangement for the metallocene.

The unit cell (with an interchange of the *b* and *c* axes) and gross structure of Cp_2Pb match the zigzag coordination polymer found by Panattoni, although there are differences in detail (Table 2). The structure consists of an infinite chain of lead atoms linked by bridging η^5 rings; an η^5-terminal ring is also present on each metal. It became apparent during the refinement of the low-temperature data set that the appropriate space group was not the same as that used in the original structure. Panattoni[3] identified an orthorhombic cell with either *Pnma* or $Pna2_1$ (both have the same systematic absences) as the choice of space groups. Refinement of the structure in the former space group requires that a disordered bridging cyclopentadienyl ring reside on a mirror plane. Since a Fourier difference map phased on the room temperature data revealed a ring of electron density

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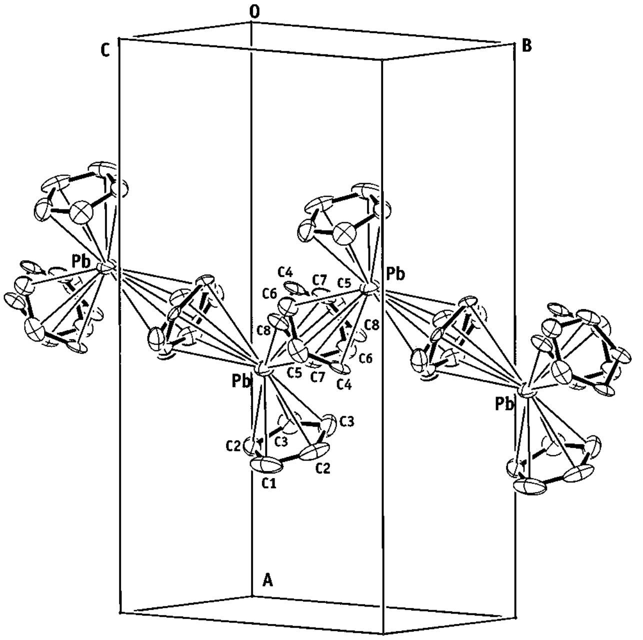

Figure 2. Packing diagram of the non-hydrogen atoms of Cp_2Pb, giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 40% level.

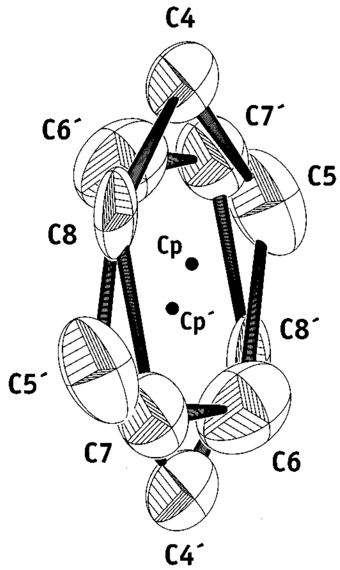

Figure 3. Disorder model of the bridging cyclopentadienyl ring. The two rings (each at 0.5 occupancy) are parallel. Cp and Cp′ represent the centroids of each ring and are 0.33 Å from each other. Thermal ellipsoids are shown at the 40% level.

that was identified as an ordered ring, the choice of $Pna2_1$ was originally considered correct.

Analysis of our intensity data indicated that *Pnma* was the proper space group. Initial attempts at anisotropic refinement in $Pna2_1$ resulted in numerous carbon atoms becoming non-positive definite, but subsequent refinement and modeling of a disordered bridging cyclopentadienyl ring in *Pnma* were successful. The centroids of the disordered rings are not on a single inversion point but are separated by 0.33 Å (Figure 3). The C−C bond distances in the bridging cyclopentadienyl group of the original structure displayed a broad range (1.29−1.54 Å); that such a spread in distances was not recognized as a consequence of disorder probably stemmed from the low quality of the data.

The metrical data determined from this reinvestigation clarify the bonding arrangements present (Table 2). The average Pb−C (terminal ring) distance of 2.736(8) Å (range: 2.718−2.75 Å) is comparable to the value of 2.76 Å in the original structure and is similar to the $Pb-Cp_{terminal}$ distances in all known plumbocene modifications. The average Pb−C (bridging ring) length of 2.96(3) Å (range: 2.94−3.00 Å) in the present refinement is notably smaller than the 3.06 Å average in the original structure. Furthermore, the range of C−C distances in the rings (1.36−1.41 Å) compares favorably with typical cyclopentadienyl C−C bond distances.[8]

Structural Implications of Bonding in Cp_2Pb. The existence of three different solid state modifications of plumbocene suggests that the conformations are highly sensitive to the local environment. Panattoni[3] proposed that the polymeric chains in plumbocene were a result of an interaction of the metal-centered lone pair of valence electrons with the π orbitals in a bridging cyclopentadienyl ring, producing sets of bonding, nonbonding, and antibonding orbitals. However, in the last 30 years polymeric chain motifs have been found in a number of metallocenes, where it is often a signature of a primarily ionic, rather than covalent, interaction. Examples are found among the main group elements (e.g., CpCs,[9] Cp_2Ca,[10] $Cp^*{}_2Ba$[11]), lanthanides (e.g., $[(Me_3Si)_2C_5H_3]_2Yb$, $[(Me_3Si)_2C_5H_3]_2Eu)$,[12] and transition metals (Cp_2Mn[13]).

The formation of polymeric chains represents an attempt by each complex to fill the coordination sphere of the respective metal as completely as possible. The presence of sufficiently bulky cyclopentadienyl rings lessens the need for intermolecular coordination, and such complexes are usually monomeric (e.g., $Cp^*{}_2Ca$,[11] $(C_5(i\text{-}Pr)_4H)_2Ba$,[14] $(C_5(i\text{-}Pr)_4H)_2Sm$,[15] $Cp^*{}_2Mn$[16]). Thus a metal-centered lone pair need not be invoked to describe the origin of the polymeric structure of plumbocene.

Conclusions

The existence of a zigzag chain modification of plumbocene has been confirmed, although it has been determined that the original structure was refined in an improper space group. Assignment of the space group *Pnma* gave satisfactory results and provided evidence for the existence of a disordered bridging cyclopentadienyl ring. Comparison of the polymeric chain structure of plumbocene with other ionic structures of the main group, transition, and lanthanide metals demonstrates that a metal-centered lone pair of electrons is not necessary to explain the nature of the bonding.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the complex Cp_2Pb is available on the Internet only. Access information is given on any current masthead page.

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