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Communication

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Application of ^{204m}Pb Perturbed Angular Correlation of γ-rays Spectroscopy in Coordination Chemistry

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Supporting Information

ABSTRACT: ^{204m}Pb perturbed angular correlation of γ-rays (PAC) spectroscopy has been applied successfully for the first time to detect the nuclear quadrupole interaction in a lead(II) coordination compound in a molecular crystal [tetraphenylarsonium lead(II) isomaleonitriledithiolate ($[AsPh_4]_4[Pb_2(\text{i-mnt})_4]$)]. The recorded parameters from a powder crystalline sample are $\nu_Q = 0.178(1)$ GHz and $\eta = 0.970(7)$. The electric field gradient (EFG) was determined at the PW91/QZ4P level including relativistic effects using the two-component zeroth-order regular approximation method for both the $[Pb(\text{i-mnt})_2]^{2-}$ monomer and the $[Pb_2(\text{i-mnt})_4]^{4-}$ dimer. Only the EFG for the latter compares favorably with the experimental data, indicating that the picture of this complex as a prototypical hemidirected coordination geometry with a stereochemically active lone pair on lead(II) is inadequate. Advantages and limitations of ^{204m}Pb PAC spectroscopy as a novel technique to elucidate the electronic and molecular structures of lead-containing complexes and biomolecules are presented.

The chemistry of lead is of interest in its own right and deserves particular attention because the molecular and electronic origins of lead toxicity are still not fully characterized.[1] A central question in the coordination chemistry of lead(II) is whether it possesses a stereochemically active lone pair originating from hybridization of the 6s and 6p atomic orbitals.[2] In this context, the compound investigated in this work has been considered to be a prototypical example of a hemidirected coordination geometry with a stereochemically active lone pair pointing to the direction not occupied by the ligands (Figure 1, left).[3]

Perturbed angular correlation of γ-rays (PAC) spectroscopy has been applied routinely in solid-state physics over the past 5 decades and, to a lesser extent, in coordination chemistry and biochemistry.[4] PAC spectroscopy belongs to the family of hyperfine interaction techniques, where the nuclear quadrupole interaction (NQI) may be determined, providing information on the local structure and, in certain cases, dynamics at the PAC probe site. The three PAC probes ^{111m}Cd, ^{199m}Hg, and ^{204m}Pb are particularly attractive because no change of the element accompanies the nuclear decay. ^{111m}Cd PAC is applied routinely in coordination chemistry and biochemistry,[4] and ^{199m}Hg PAC spectroscopy has been established over the past 10 years, although the number of applications is still limited.[5]

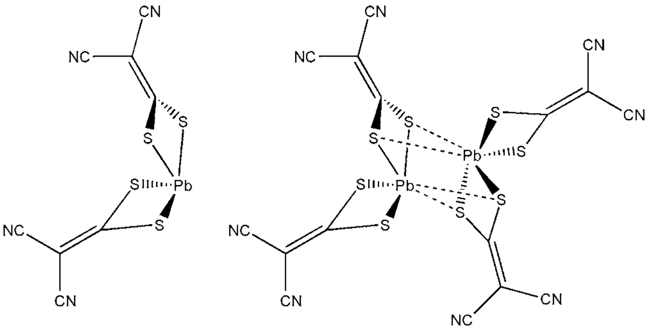

Figure 1. Models of $[AsPh_4]_4[Pb_2(\text{i-mnt})_4]$: (left) monomeric model; (right) dimeric model.

^{204m}Pb PAC spectroscopy was first applied in 1973 by Haas and Shirley[6] in investigations of inorganic compounds such as $PbCl_2$, PbFCl, PbI_2, PbO, $PbSO_4$, $PbCrO_4$, PbC_2O_4, and $Pb(SCN)_2$. Only recently was the technique revived, and additional inorganic compounds were explored.[7] No applications to molecular crystals or applications in biochemistry have been published yet in peer-reviewed journals, although a promising attempt to determine the NQI in lead(II)-substituted azurin was carried out by Heinrich.[7] In this Communication, we present the first application of ^{204m}Pb PAC to a molecular crystal, in the sense that it possesses a full molecular entity in the unit cell rather than the periodic crystalline structure of the inorganic compounds investigated previously. The relatively short half-life of ^{204m}Pb ($T_{1/2} = 67$ min) imposes constraints on the time available for sample preparation, and so far only $[AsPh_4]_4[Pb_2(\text{i-mnt})_4]$ has provided a PAC spectrum that could be interpreted reliably and an X-ray diffraction pattern from the powder crystalline sample that agrees with the expected molecular structure.[3] Recently, it was demonstrated that the structure of $[AsPh_4]_4[Pb_2(\text{i-mnt})_4]$ may be more complex[1] than previously assumed (Figure 1, right). The asymmetric unit is composed of a monomer with two tetraphenylarsonium counterions, and while the unit cell contains two monomers, these are not in proximity; it is between two monomers in adjacent unit cells

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that several important short contacts occur. The dinuclear dimeric structure is characterized by hexacoordination of lead(II).

Because the NQI is particularly sensitive to the local molecular and electronic structures at the site of the PAC probe, ^{204m}Pb PAC spectroscopy combined with density functional theory (DFT) calculations of the spectroscopic property may elucidate if the electronic structure reflects the monomeric or dimeric structure.

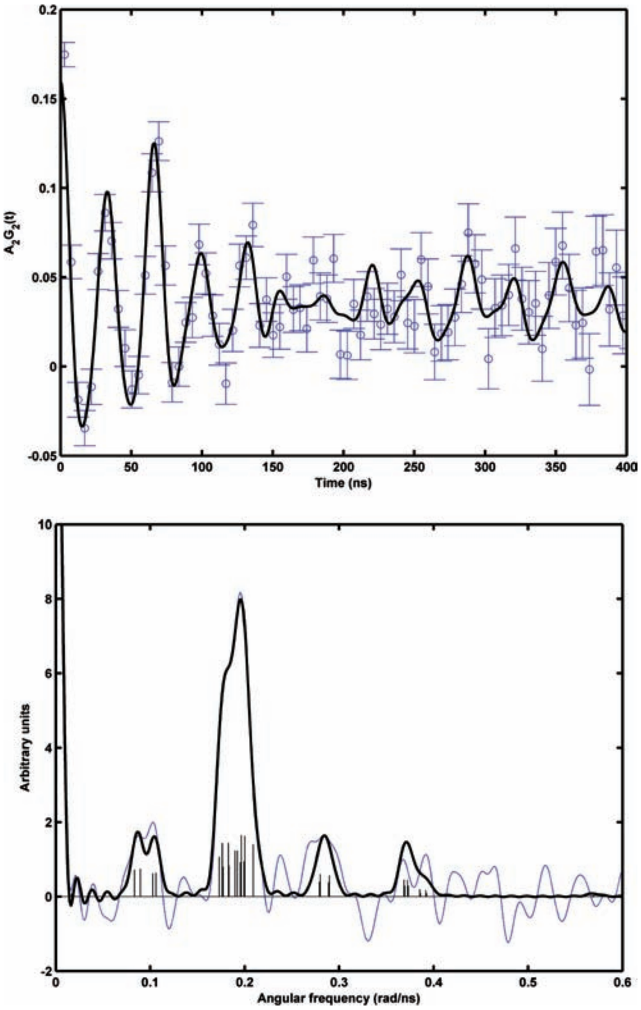

Figure 2. ^{204m}Pb PAC spectroscopic data for powder crystals of $[AsPh_4]_4[Pb_2(i\text{-}mnt)_4]$. Top: Experimentally determined PAC spectrum (blue) and fit (bold line). Bottom: Fourier transformation of the experimental data (thin line) and fit (bold line). The positions and relative intensities of the 36 lines, given the fitted ν_Q = 0.178(1) GHz and η = 0.970(7), are presented as vertical bars.

In Figure 2, the ^{204m}Pb PAC data are presented. The data are fitted reliably with one NQI, indicating that only a single lead(II) coordination geometry is present in the sample.

The electric field gradient (EFG) was calculated using the *ADF*[8] program package with the PW91[9] functional and the QZ4P basis set,[10] treating relativistic effects at the zeroth-order regular approximation (ZORA) level[11] including spin–orbit coupling and a small component density.[12] This approach has been demonstrated to adequately reproduce fully relativistic four-component CCSD(T) calculations of EFGs for Hg-halides.[13] Only a very limited number of quantum mechanical calculations of EFGs in lead(II)-containing compounds are found in the literature.[7,14] The calculated EFGs for the two model systems are V_{zz} = 2.32 au, η = 0.59 for $[Pb(i\text{-}mnt)_2]^{2-}$ and V_{zz} = 1.51 au, η = 0.77 for $[Pb_2(i\text{-}mnt)_4]^{4-}$. The prior EFG gives a too large V_{zz} and a too low η compared to the experimentally derived value (V_{zz} = ±1.72(8) au, η = 0.970(7), using Q = 0.44(2)[15]), whereas the latter agrees reasonably well with experiment. Thus, the structure of $[AsPh_4]_4[Pb_2(i\text{-}mnt)_4]$ cannot be characterized as a monomeric hemidirected coordination geometry with a stereochemically active lone pair on lead(II) but is adequately represented by the dimeric structure.

^{204m}Pb PAC spectroscopy may be complicated because of the fact that ^{204}Pb has I = 4 in the intermediate nuclear level of the detected γ–γ cascade and therefore gives complex spectra with 36 lines (7 for the special case η = 0) in the Fourier transform of the PAC spectrum. The expression for the perturbation function is known,[12] and only two parameters (ν_Q and η) are required to reproduce the positions and intensities of the lines. With this large number of lines, however, even limited line broadening may lead to coalescing peaks, potentially obscuring the interpretations of the spectroscopic data. In a crystalline sample, this is usually not a serious problem, but minor structural variations of lead(II)-containing complexes or metal-ion binding sites in proteins may lead to line broadening. Similarly, rotational diffusion of the molecules in solution will give rise to line broadening, and therefore ^{204m}Pb PAC studies may be limited to immobilized molecules, e.g., frozen samples, or to very large biomolecules, which display relatively slow rotational diffusion. Finally, multiple coexisting species will give rise to a set of 36 peaks each, which may complicate the interpretation. A particular advantage of ^{204m}Pb PAC spectroscopy is the relatively long half-life of the intermediate level (265 ns), providing good frequency resolution. Advantages and limitations of PAC spectroscopy, in general, may be found in the literature.[11,12]

Only a limited number of spectroscopic techniques provide information on the coordination geometry of Pb(II) in complexes and in biomolecules. PAC spectroscopy complements extended X-ray absorption fine structure (EXAFS) and ^{207}Pb NMR spectroscopy well because only small amounts of material are required and because the EFG is particularly sensitive to changes in ligand–metal–ligand angles, whereas EXAFS is sensitive to the metal–ligand distances. UV–vis absorption spectroscopy is highly useful[16] but limited to the ligand-to-metal charge-transfer bands appearing, for example, from the sulfur to lead coordination.

In the context of elucidating the presence of a potential stereochemically active lone pair of lead(II), ^{204m}Pb PAC spectroscopy may offer particular advantages: In a simple picture, the EFG originates mainly from the partial occupation of the 6p orbitals of lead(II) because electrons in the 6s orbital give no EFG in a pure atomic orbital picture due to the symmetry of the s orbitals. Therefore, sp hybridization will give rise to an increase of the EFG, and large EFGs may be a hallmark of the presence of a stereochemically active lone pair, although the EFG will, of course, depend on the complete coordination geometry.

In summary, the present work demonstrates that ^{204m}Pb PAC spectroscopy may provide information on the coordination geometry of lead(II), complementing other techniques commonly applied to study lead coordination compounds. This is of interest both in inorganic chemistry, where coordination compounds and complexes in solution may be characterized at the atomic and electronic levels, and in bioinorganic chemistry, where the binding of lead to both proteins and nucleic acids is of considerable importance in toxicity and in the function of so-called leadzymes.[1,17]

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, a plot of the powder X-ray diffraction data, and a table with fitted PAC parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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