EPR-Spectroscopic Characterization of Persistent Germyl-Substituted Pb(III)- and Sn(III)-Radicals

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- Supplementary Information -

Calculation of spin populations from the isotropic and the dipolar parts of the ^{13}C hyperfine couplings. The isotropic hyperfine coupling is a direct measure of the spin population in s-type orbitals ρ_s, whereas the anisotropic part T of the hyperfine coupling allows for the calculation of the spin population in p-type orbitals ρ_p.[S1] For an unpaired electron (free electron, g_e=2.0023) on a ^{207}Pb-nucleus with a spin population of ρ_s=1 in an s-type orbital one would observe an isotropic hyperfine coupling constant of a_0=2908.49 mT. For ^{117}Sn $|a_0|$ is given as 1497.98mT. Including a correction for the difference in the g values (e.g. $g_{iso}(PbHGe_3)=2.084$), the spin populations in s-type orbitals can thus be estimated as:

$$\mathbf{8}: \rho_s = A_{av}/a_0 \cdot g_e/g_{iso} = 46.30\mathrm{mT}/2908.49\mathrm{mT} \cdot 2.0023/2.084 \approx 1.5\% \qquad \text{(S1a)}$$

9: $\rho_s = A_{av}/a_0 \cdot g_e/g_{iso} = 48.30\text{mT}/2908.49\text{mT} \cdot 2.0023/2.074 \approx 1.6\%$ (S1b)

10: $\rho_s = A_{av}/a_0 \cdot g_e/g_{iso} = 63.70\text{mT}/2908.49\text{mT} * 2.0023/2.0013 \approx 2.2\%$ (S1c)

For comparison:

PbHyp$_3$: $\rho_s = A_{av}/a_0 \cdot g_e/g_{iso} = 84.30\text{mT}/2908.49\text{mT} * 2.0023/2.1143 \approx 2.7\%$ (S1d)

11(^{117}Sn): $|\rho_s| = A_{av}/a_0 \cdot g_e/g_{iso} = 66\text{mT}/1497.98\text{mT} * 2.0023/2.051 \approx 4.3\%$ (S1e)

For comparison:

SnHyp$_3$ (^{117}Sn): $|\rho_s| = A_{av}/a_0 \cdot g_e/g_{iso} = 60.10\text{mT}/1497.98\text{mT} * 2.0023/2.046 \approx 3.9\%$ (S1f)

Estimation of the inversion barrier for Hge$_3$Pb (8)

All calculations were done using the Gaussian09 program (Revision A.02).[S2] The geometry of Hge$_3$Pb (**8**) was optimised on Hartree-Fock level treating electrons on C, H and Si explicitly and employing following basis-sets coming with Gaussian09:

C, H: 3-21G

Si: 6-31+G*

Ge and Pb atoms were described with quasi-relativistic Stuttgart-Dresden pseudo-potentials 28-MWB and 78-MWB and the published (5s5p1d)[3s3p1d][S3a] and (5s5p2d)[3s3p2d][S3b] basis-sets, respectively. The resulting (C_{3v}-symmetric) structure was confirmed to be a local minimum on the energy hypersurface by a subsequent frequency calculation (no imaginary frequency).

The frequency analyses of the C_{3v}-minimum revealed a low-energy vibrational mode which predominantly describes the motion of the Pb-atom perpendicular to the Ge$_3$-plane (Ge$_3$Pb-inversion). ***The energy corresponding to this mode is 79 cm^{-1} or 0.95 KJmol^{-1}***.

In a second step a geometry-optimisation was done imposing local D_{3h}-symmetry on the Ge_3Pb backbone (by fixing all Ge-Pb-Ge angles to 120°C). The optimised structure (1 imaginary frequency) still has only C_{3v}-symmetry.

On both resulting structures single-point calculations were done using augmented basis-sets for Si, Ge and Pb:

Si: aug-cc-pvtz

Ge: basis(28MWB) augmented to be (6s6p2d)[4s4p2d]

exponents of the added basis functions: s: 0.01; p: 0.007; d: 0.08

Pb: basis(78MWB): augmented to be (6s6p2d1f)[4s4p2d1f]

exponents of the added basis functions: s: 0.01; p: 0.008; f: 1.0

The calculated energy difference between the C_{3v} minimum and the planar conformation is 0.063 a.u. or 16.5 KJmol^{-1}

[S1] J. A. Weil, J. R. Bolton, J. E. Wertz, *Electron Paramagnetic Resonance – Elementary Theory and Practical Applications*, Wiley, New York, **1994**.

[S2] Gaussian09 Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[S3] (a) (Pb) W. Kuechle, M. Dolg, H. Stoll, H. Preuss, *Mol. Phys.* **1991**, *74*, 1245; (b) (Ge) A. Bergner; M. Dolg; W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431.