Superposition Model Analysis of NMR Data for $TlPbI_3$

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Z. Naturforsch. **43a,** 1072–1074 (1988); received October 25, 1988

Chemical shift anisotropies of ^{205}Tl and ^{207}Pb in $TlPbI_3$ from the literature are shown to be determined by the distortions of the MI_n coordination polyhedra. Application of the superposition model results in very good agreement with the patterns calculated from crystal structure data with an exponent $t = 24$ for the dependence on bond distance and intrinsic shift parameters of -83.5 and -600 ppm/distortion for ^{205}Tl and ^{207}Pb resp., larger than the value for ^{29}Si in Mg_2SiO_4. The high value for the exponent suggests that mechanisms proportional to a higher power of overlap of electron density dominate whereas purely electrostatic mechanisms are of minor importance.

Introduction

Recently it was shown that the chemical shift anisotropy of ^{29}Si as well as the quadrupole splitting patterns for ^{25}Mg in the mineral forsterite (Mg_2SiO_4) at least for their major parts can be accounted for by distortions of first coordination spheres [1]. Thus, just like for the zero-field splitting patterns of 3 d ions they could very well be reproduced by application of the superposition model [2], and like in the cases of the d^5 ions Mn^{2+} and Fe^{3+}, the dependence of the intrinsic parameters (i.e. the resonance data per unit distortion) on bond length could be approximated by an exponent $t = 7$, but a three times higher exponent could also not be excluded for the NQR data of ^{25}Mg.

Recently the chemical shift tensors for ^{205}Tl and ^{207}Pb in $TlPbI_3$ were determined [3]. Since a rather accurate crystal structure determination also exists for this compound [4], these NMR data for very heavy nuclei can also be subjected to a superposition analysis. The authors of the NMR study already noted a very close relation of the directions of the z axes of the chemical shift tensors with the shortest bond directions within the MI_n polyhedra with $n = 8$ for M = Tl and $n = 6$ for Pb [4], suggesting that also in this case the distortions of the first coordination spheres largely influence the patterns of the chemical shift anisotropies. But only a detailed quantitative analysis is a critical test of the validity of the superposition model in each case and allows an evaluation of the best choice of the exponent t for the dependence on bond distance as the second free variable in this model in addition to the intrinsic parameters. Since the Pb^{2+} and Tl^+ ions are in sites of monoclinic and orthorhombic site symmetry, respectively, the principal axes of their chemical shift tensors are not determined by symmetry, and thus critical tests are possible in both cases.

We undertook such an analysis for the data of both nuclei and obtained very good agreement with the same choice of the exponent t. Its very high value suggests that also for these NMR shifts mechanisms based on overlap of electron densities between central ion and ligands dominate whereas purely electrostatic mechanisms are of minor importance.

Results

^{207}Pb

Due to the monoclinic site symmetry, two of the principal axes of the chemical shift tensor for ^{207}Pb are restricted to the $b-c$ plane whereas the third one must be parallel to the a axis. The results show that the y axis of smallest shift is parallel to a, whereas the x and z axes are ±30 and ±60°, respectively, away from the c axis [3]. Thus there is a choice of which pattern of the two magnetically nonequivalent Pb^{2+} to associate with which site. This choice was already

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made in the NMR investigation based on the directions of the shortest Pb–I bonds [3]. A comparison of the NMR pattern with that calculated from the crystal structure data for the b–c plane thus gives a complete picture of the degree of agreement in both sizes and orientations for all three principal values. As was previously done for the zero-field splitting patterns of 3 d ions [5], we compare them in the dimensionless units of distortion, i.e. the fraction of a ligand at average bond distance that (for positive values of distortion) seems to be acting in addition to the actual number corresponding to a compression or (for negative values) seems to be missing due to dilatation along a particular direction. This results in the shift and distortion patterns d_s and d_c, respectively:

$$d_s = \frac{\delta - \delta_{\text{iso}}}{\bar{\delta}}, \qquad (1)$$

$$d_c = \tfrac{1}{2} \sum_i (3\cos^2\theta_i - 1) \left(\frac{R_0}{R_i}\right)^t \qquad (2)$$

with $\bar{\delta}$ the intrinsic splitting parameter and θ_i the angle between the Pb–I_i bond direction and the individual direction considered. The summation runs over all I ligands of Pb.

Alternatively, the shift anisotropy could also be decomposed into its axial and orthorhombic components δ_a and δ_r to emphasize the analogy to the zero-field splitting parameters b_2^0 and b_2^2 of transition-metal ions, as was done for the NMR data of ^{29}Si in Mg_2SiO_4 [1].

The shift and distortion patterns are compared in Figure 1. The intrinsic splitting parameter $\bar{\delta} = -600.2$ ppm/distortion together with $t = 24$ results in agreement for the three principal values within 1% and a deviation of the principal axes of 1.9 ± 0.7°. No errors are given for the orientations of x and z obtained from the NMR data, but it is obvious from Fig. 5 of [3] that the uncertainty is at least as large as this deviation. The limits of error for the distortion pattern are 4.9 and 3.0% for z and x, respectively, from the crystal structure data. Thus within the limits of error the agreement is complete.

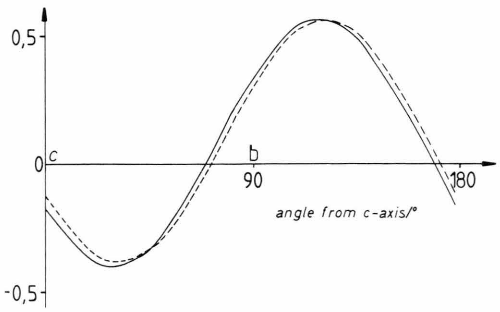

Fig. 1. Comparison of the distortions resulting from the crystal structure data (d_c, dashed curve, calculated with $t = 24$ according to (2)) and from the chemical shift anisotropy for ^{207}Pb in $TlPbI_3$ with $\bar{\delta} = -600$ ppm/distortion according to (1), solid curve. The ordinate gives the distortion = fraction of a ligand at normal bond distance (see text).

^{205}Tl

Due to the orthorhombic site symmetry, only one spectrum is obtained for this ion, and the principal values are aligned along the crystal axes. Since, however, there is no definite association of a particular crystal axis with any one of the three principal axes of the shift tensor, a critical test is again possible. Like for ^{207}Pb an exponent $t = 24$ is again required to obtain the best agreement for all three axes, whereas smaller exponents interchange the axes in the distortion pattern. With an intrinsic shift parameter $\bar{\delta} = -83.5$ ppm/distortion, agreement within 1% is obtained for all three axes, whereas the uncertainties in the distortion pattern from the crystal structure data [4] range between ±1.8% for x along the a axis and ±3.4% for y along b. Thus once again perfect agreement within the limits of experimental error is obtained with the same choice of the exponent t for the dependence on bond distance.

Discussion

Due to lack of experimental data for the chemical shift anisotropies of ^{205}Tl and ^{207}Pb in other compounds it is not yet possible to compare these results with others for the same nuclei. However, the complete agreement of the exponent t in our view clearly indicates that most likely analogous results can be expected for other systems also. The unexpectedly high exponent $t = 24$ is a clear indication that as for the zero-field splittings of transition-metal ions (at least with heavier ligands) purely electrostatic mechanisms are of minor importance. The dominant mechanism(s) appears to be proportional to a higher power of the overlap of electron density between central ion and ligands. Certainly this is a very demanding challenge for theoreticians to perform quantum-mechanical calculations analogous to those existing for the mechanisms of zero-field splitting for transition-metal ions [6].

The reason for the large difference in the intrinsic shift parameters for these ions by a factor for more than 7 is not yet understood, but two obvious possibilities exist:

a) The bond distances differ considerably. From the average bond distances R_0 of 320.7 and 366.6 pm for Pb and Tl, respectively, a "compression factor" of 25 is calculated with the exponent $t = 24$, much larger than the actual ratio.

b) The ionicity of the bonds is somewhat larger for Tl^+ than for Pb^{2+}. If there is a significant increase of the intrinsic parameters with the degree of covalency, this could also explain the observed differences. Results for trivalent Tl and for systems with more electronegative ligands like F^- and O^{2-} would be extremely interesting in this connection.

Comparisons with results for lighter nuclei are possible. Interestingly, the value of -37 ppm/distortion for ^{29}Si in Mg_2SiO_4 [1] is in the same range as that for ^{205}Tl in $TlPbI_3$. This value is, of course, also dependent on the choice of the exponent t. While $t = 7$ was chosen, a value of 11 was also possible. However, for the quadrupolar splitting of ^{25}Mg an exponent in the range of 20, comparable to the one used here, appeared to be the best choice, but was considered to be unlikely at that time since it was an isolated observation. Considerably more quadrupolar splitting data are available for ^{27}Al and are at present evaluated. Evaluation of chemical shift anisotropies for ^{111}Cd in a larger number of compounds is also underway.

Acknowledgement

We thank Mr. K. P. Such for computer evaluation of the distortion patterns from crystal structure data. We also acknowledge financial support of our cooperation by the Stiftung Volkswagenwerk.

We also acknowledge financial support of our cooperation by the Stiftung Volkswagenwerk.

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