Inorg. Chem. **1994,** *33,* 407–408

Characterization of the $J(^{115}\text{In},^{31}\text{P})$ Tensor for a 1:1 Adduct of Indium Tribromide and a Triarylphosphine

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Received July 14, 1993

NMR studies of quadrupolar nuclei in solution are often hampered by broad peaks which result from efficient quadrupolar relaxation. This problem is particularly acute when the quadrupolar nuclei reside at a site where the electric field gradient (EFG) is nonzero (*i.e.*, where the symmetry is less than T_d or O_h).[1] Furthermore, the NMR spectra of neighboring spin $^1/_2$ nuclei will generally not exhibit resolvable splittings due to indirect spin–spin coupling (J) with quadrupolar nuclei because of their short relaxation times.[2–4] These problems are illustrated by indium, where both naturally occurring isotopes, ^{113}In (4.3%) and ^{115}In (95.7%), are spin $^9/_2$, with nuclear quadrupole moments exceeding those of all other naturally occurring isotopes of the main group elements.[5] As a result, indium NMR studies have been mainly confined to the approximately tetrahedral tetrahaloindate anions and pseudooctahedral complexes.[6] The only reports in the literature of spin–spin coupling constants involving indium failed to observe resolvable splittings.[7]

The problem of short relaxation times can in part be circumvented by carrying out NMR studies on solid samples.[8] Here we report the first observation of splittings due to $^1J(\text{In,P})$. The ^{31}P CP/MAS NMR spectrum of solid tribromo(tris(4-methoxyphenyl)phosphine)indium(III), $\text{Br}_3\text{In}\cdot\text{P}(4\text{-}(\text{CH}_3\text{O})\text{C}_6\text{H}_4)_3$ (**1**), prepared from indium(III) bromide and tris(4-methoxyphenyl)phosphine,[9] is shown in Figure 1. The spectrum was obtained at 81.033 MHz on a Bruker MSL-200 NMR spectrometer (B_0 = 4.7 T). The ^{31}P NMR spectrum consists of 10 equally spaced peaks indicating $^1J(^{115}\text{In},^{31}\text{P}) = 1109 \pm 9$ Hz. The only other report of $^1J(^{115}\text{In},^{31}\text{P})$ of which we are aware comes from Adolphi, Conradi, and Buhro,[7d] who inferred $^1J(^{115}\text{In},^{31}\text{P}) \approx 350$ Hz from the broad, featureless ^{31}P NMR Gaussian peak ($\nu_{1/2} \approx 3900$ Hz), observed in MAS spectra of indium phosphide. Unresolved $^{115}\text{In},^{31}\text{P}$ indirect spin–spin coupling may also in part be responsible for the different ^{31}P NMR line widths observed for thin films of the semiconductor $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$.[7e] Qualitatively, the ^{31}P NMR peaks resulting from indium-rich clusters, *e.g.*, GaIn_3P, were found to be significantly broader than those resulting from gallium-rich clusters.

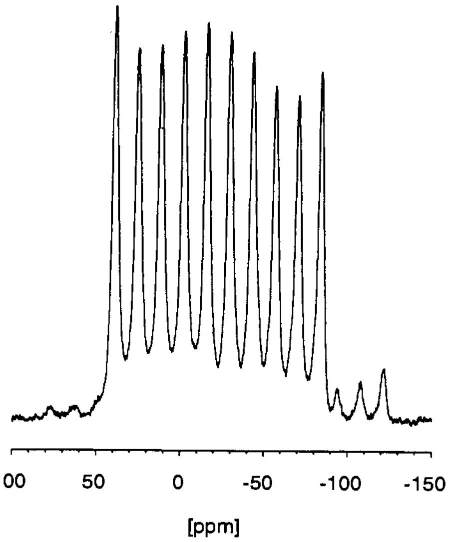

Figure 1. 81.033-MHz ^{31}P NMR spectrum of solid $\text{Br}_3\text{In}\cdot\text{P}(4\text{-}(\text{CH}_3\text{O})\text{-}\text{C}_6\text{H}_4)_3$ (**1**), obtained with CP and MAS (ν_R = 3.0 kHz), a recycle delay of 8 s, and a contact time of 5 ms. 120 free induction decays were acquired. The three small peaks flanking the high- and low-frequency peaks are spinning sidebands.

The reduced one-bond spin–spin coupling constant,[10] $^1K(\text{In,P}) = 10.35 \times 10^{21}$ N A^{-2} m^{-3}, observed for **1** is significantly larger than the corresponding values of $^1K(\text{B,P})$, $^1K(\text{Al,P})$ and $^1K(\text{Ga,P})$ in related boron, aluminum, and gallium adducts; $^1K(\text{B,P}) \approx 1.0 \times 10^{21}$, $^1K(\text{Al,P}) \approx 2.0 \times 10^{21}$, and $^1K(\text{Ga,P}) \approx 6.5 \times 10^{21}$ N A^{-2} m^{-3}.[11,7c,9b] Qualitatively, it is clear that $K(\text{M,P})$ increases as the atomic number, Z, of the group 13 metal increases. Increases of $^1K(\text{M,X})$ with Z_M in a series of isostructural compounds is a general observation.[12] Although the origin of the Z-dependence of K is not known with certainty, it is interesting to point out that the importance of the Fermi-contact mechanism is expected to increase with Z because $|\Psi_\text{ns}(0)|^2$ increases on descending any group in the periodic table.[12] Similarly, the importance of the spin–dipolar and orbital mechanisms is expected to depend on $\langle r^{-3}\rangle_\text{np}$, which also changes periodically with atomic number.[12] That is, each of the three important mechanisms for nuclear

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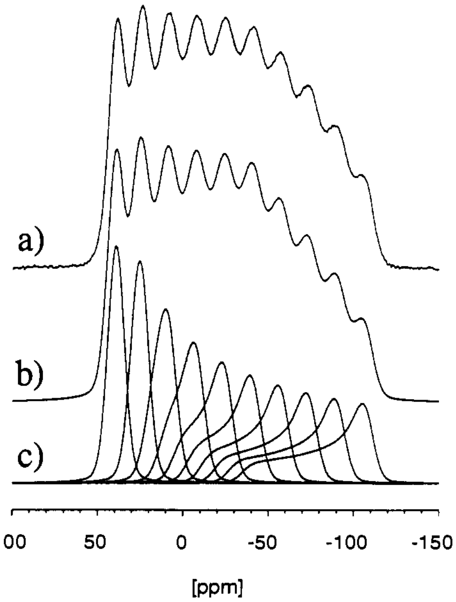

Figure 2. 81.033-MHz ^{31}P NMR spectra of a static sample of **1**: (a) experimental spectrum obtained with CP, a recycle delay of 30 s, and 2256 scans; (b) calculated spectrum (see text for parameters used and further details); (c) calculated powder line shapes for each of the 10 allowed ^{31}P NMR transitions of **1**. Note that the effective anisotropy of the lowest frequency transition is $\Delta\nu_{CS} - (27/2)R_{eff}$ while that of the highest frequency transition is $\Delta\nu_{CS} + (27/2)R_{eff}$, where $\Delta\nu_{CS} = \nu_{\perp} - \nu_{\parallel}$.

spin–spin coupling increases with Z. However, on the basis of rather crude calculations and qualitative arguments, it is generally accepted that the Fermi-contact mechanism is the most important.

The ^{31}P NMR spectrum of a nonspinning sample of solid **1** is shown in Figure 2, together with a theoretical spectrum. In order to calculate the theoretical spectrum, it is necessary to consider the anisotropic chemical shift, direct dipolar coupling, and indirect coupling interactions.[13] The analysis of the powder spectrum is greatly simplified by the presence of a 3-fold axis of symmetry along the In–P bond.[14] This element of symmetry requires that both the phosphorus chemical shift tensor, $\boldsymbol{\delta}(P)$, and the indium–phosphorus indirect spin–spin coupling tensor, $\mathbf{J}(In,P)$, be axially symmetric.[13e,15] The ^{31}P NMR spectrum in Figure 2b was calculated using the following parameters: $\delta_{\parallel} = 2 \pm 1$ ppm, $\delta_{\perp} = -34 \pm 1$ ppm, and $R_{eff} = 230 \pm 50$ Hz. Here $R_{eff} = R_{dd} - \Delta J/3$, where $R_{dd} = (\mu_0/4\pi)\gamma_{In}\gamma_P r_{In,P}^{-3}(\hbar/2\pi)$ and $\Delta J = J_{\parallel} - J_{\perp}$. From the X-ray diffraction results on **1**, $r_{In,P} = 2.583 \times 10^{-10}$ m;[14] thus $R_{dd} = +623$ Hz and $\Delta J = +1178 \pm 150$ Hz or -2558 ± 150 Hz. Analysis of the static ^{31}P NMR powder pattern also indicates that $^{1}J(^{115}In,^{31}P)$ and R_{eff} have the same sign. Since the sign of $^{1}J(^{11}B,^{31}P)$ is positive in analogous compounds,[11] it is reasonable to assume that $^{1}J(^{115}In,^{31}P)$ is positive;[12] thus, the smaller value of ΔJ is preferred. The conclusion is that ΔJ is at least comparable in magnitude to J_{iso}. It is important to emphasize that generally it is difficult to experimentally measure anisotropies in J tensors; few reliable values are available in the literature.[13e,f,16] In the case of **1**, it is the symmetry along the In–P bond axis that makes a reliable analysis feasible. The implication of a nonzero ΔJ is that spin–spin coupling mechanisms other than the Fermi-contact mechanism must play an important role in the transmission of spin information between the two coupled nuclei.[12,15a,16]

Two additional features of the ^{31}P CP/MAS spectrum shown in Figure 1 are worthy of comment. First, it is important to emphasize that the splittings between each of the adjacent peaks are the same within experimental error (*i.e.*, 1109 ± 9 Hz). Typically, unequal splittings are observed in MAS NMR spectra of spin $^1/_2$ nuclei which are spin–spin coupled to quadrupolar nuclei.[8] In the case of **1**, we conclude that the distortion parameter "d" is less than 50 Hz; thus, the ^{115}In nuclear quadrupolar coupling constant, $\chi(^{115}In)$, is less than 32 MHz.[17] The relatively small value of $\chi(^{115}In)$ for **1** is in agreement with the predictions of Brill[18] and Bancroft and Sham.[19] Also, it is interesting to note that for trimethylindium phosphines very large quadrupolar coupling constants are observed (*e.g.*, for Me_3InPMe_3, $\chi(^{115}In) = 643.01$ MHz).[20]

The second feature of the MAS spectrum of Figure 1 worthy of comment is the relative peak heights of the 10-line multiplet. Although the integrated intensities of each of the 10 peaks are identical, the outer peaks associated with the transitions $|^1/_2, ^9/_2\rangle \rightarrow |{-}^1/_2, ^9/_2\rangle$, and $|^1/_2, -^9/_2\rangle \rightarrow |{-}^1/_2, -^9/_2\rangle$ are sharper ($\nu_{1/2} \approx 280$ Hz) than the inner peaks, for example, those associated with indium spin states of $\pm^7/_2$ ($\nu_{1/2} \approx 310$ Hz). Similar observations have been made in solution NMR studies (*e.g.*: ^{19}F NMR spectra of BiF_6^-, $I(^{209}Bi) = ^9/_2$; ^{17}O NMR spectra of TcO_4^-, $I(^{99}Tc) = ^9/_2$),[3,21] and attributed to the longer lifetimes of the $\pm^9/_2$ spin states. It is not clear how one would obtain exact expressions for the relative probabilities of single- and double-quantum transitions of a spin $^9/_2$ nucleus in the solid state; however, this is certainly beyond the scope of this communication.

In summary, compound **1** provides the first example of a spin-pair I,S for which it is possible to determine the I,S indirect spin–spin coupling tensor from the spin $^1/_2$ NMR powder spectrum of a nonspinning I,S spin-pair where the spin $S > ^1/_2$. In particular, $J(^{115}In,^{31}P)_{iso}$ in a 1:1 adduct of the type $X_3In{\cdot}PR_3$ exceeds 1 kHz. Also, the large anisotropic $\mathbf{J}(^{115}In,^{31}P)$ tensor in **1** clearly indicates the importance of nuclear spin–spin coupling mechanisms other than the Fermi-contact mechanism. Finally, our results confirm that indium nuclear quadrupolar coupling constants in these systems are rather small, as previously predicted.

Acknowledgment. We thank J. Clyburn and Professor N. Burford for helpful discussions concerning the preparation of **1** and M. D. Lumsden, C. Kirby, S. Kroeker, and G. Wu for their interest in this work. This research was supported by the NSERC of Canada.

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