

Solid-state ^{115}In NMR study of indium coordination complexes†

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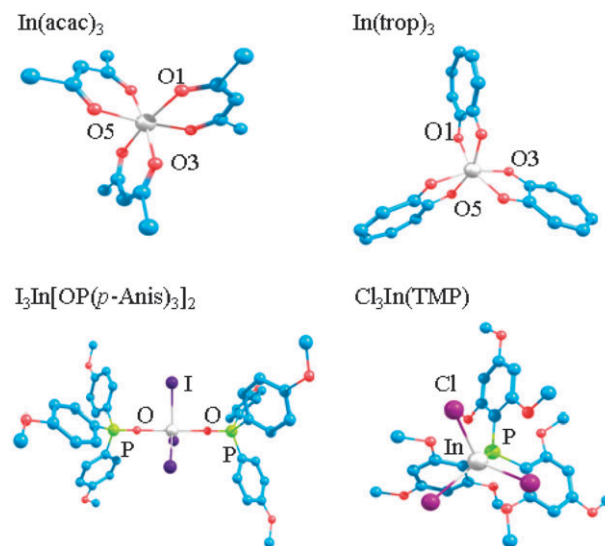
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The feasibility of solid-state ^{115}In NMR studies is demonstrated by an examination of four different coordination complexes: indium(III) acetylacetonate, indium(III) tris(tropolonato), indium(III) triiodide bis(tris(4-methoxyphenyl)phosphine oxide) and indium(III) trichloride tris(2,4,6-trimethoxyphenyl)phosphine. The results provide information about the electric field gradients and magnetic shielding at the indium nuclei through the nuclear quadrupolar and chemical shift parameters, respectively. The C_Q values in these four complexes range between 106.0 ± 2.0 and 200.0 ± 4.0 MHz, while the magnetic shielding anisotropies fall in the range from 85 ± 15 to 550 ± 60 ppm. Finally, this research demonstrates that solid-state ^{115}In NMR studies are facilitated by performing experiments at the highest possible magnetic-field strengths, and that NMR offers a promising tool for the characterization of indium compounds.

Indium coordination complexes find many important applications ranging from materials chemistry to nuclear medicine.^{1–5} One well-known example, indium(III) acetylacetonate, $\text{In}(\text{acac})_3$, is a versatile precursor for preparing a variety of materials, including pure or doped In_2O_3 nanocrystals used as transparent semiconductors.¹ $\text{In}(\text{acac})_3$ is also a promising co-catalyst in advanced organic synthesis.² The radioactive nuclide, ^{111}In , incorporated in indium(III) tris(tropolonato), $\text{In}(\text{trop})_3$, is commonly used as a labeling agent in diagnostic nuclear medicine.³ The adducts of indium trihalide or indium trialkyl compounds with phosphine ligands are environment-friendly, single-source, precursors for preparing a wide range of InP-based semiconductors.⁴ Indium complexes are reasonably well studied in the solution state and are usually characterized by coordination numbers ranging from two to eight.⁵ However, structural information for these complexes in the solid state is still scarce.

Here we demonstrate that ^{115}In NMR spectroscopy is an ideal technique to characterize indium compounds in the solid state. Indium-115 is a spin-9/2 nucleus with a quadrupolar moment, $Q = 81.0 \text{ fm}^2$, largest of all naturally occurring isotopes of the main group elements.⁶ The large value of Q



Scheme 1 Molecular structures.

usually results in proportionally large nuclear quadrupolar coupling constants, $C_Q(^{115}\text{In})$, for indium compounds, which lead to very broad NMR line shapes that are difficult to acquire experimentally. Previously, solid-state ^{115}In NMR studies have been mainly confined to the tetrahedral tetrahaloindate, InX_4^- , and octahedral hexahaloindate, InX_6^{3-} , anions, for which symmetry ensures that the electric field gradient, EFG, at the In nucleus is small resulting in $C_Q(^{115}\text{In})$ values that are typically less than 50 MHz.⁷ In the past, $C_Q(^{115}\text{In})$ values greater than 50 MHz have been determined using either nuclear quadrupole resonance spectroscopy or microwave spectroscopy; for example, see ref. 8.

In an earlier ^{31}P NMR study of solid $\text{Br}_3\text{In}-\text{P}(\text{4-C}_6\text{H}_4\text{(OCH}_3)_3)_3$, we found negligible residual $^{115}\text{In}-^{31}\text{P}$ dipolar coupling in spectra acquired with magic angle spinning (MAS) and predicted that $C_Q(^{115}\text{In})$ in this complex must be less than 32 MHz.⁹ This observation suggested that 1 : 1 adducts of indium trihalide and triarylphosphine ligands should be amenable to investigation by solid-state ^{115}In NMR spectroscopy.

For non-integer spin quadrupolar nuclei, the central NMR transition, $m_1 = 1/2 \leftrightarrow m_1 = -1/2$, is not perturbed by the first-order quadrupolar interaction.¹⁰ In second-order, the breadth of central transition is inversely proportional to the magnetic field, B_0 ;¹⁰ thus, one expects linewidths that scale as B_0^{-1} (in Hz) or B_0^{-2} (in ppm). The purpose of this contribution is to demonstrate the feasibility of acquiring ^{115}In NMR spectra of indium coordination complexes in solids where the EFG at the In nucleus is significant. To acquire broad central transition powder patterns

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† Electronic supplementary information (ESI) available: Sample preparation, NMR experimental details, NMR spectra acquired at 11.75 T, ZORA DFT calculation details and single-crystal X-ray diffraction data for $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_3]_2$ CCDC 699098 and $\text{Cl}_3\text{In}(\text{TMP})$ CCDC 699099. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814326a

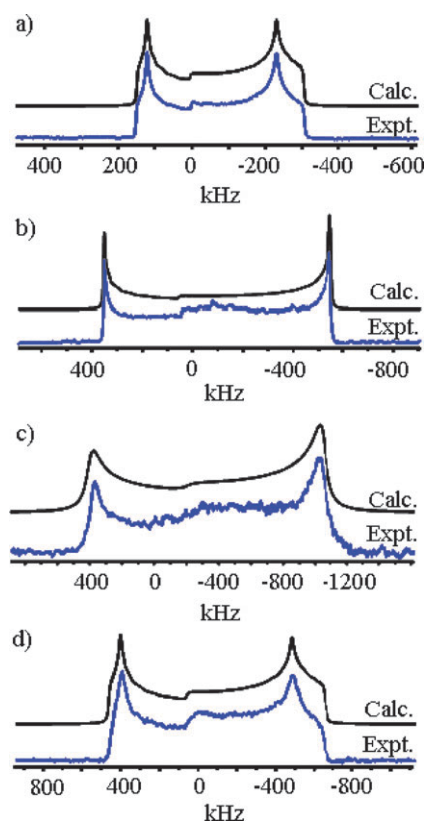


Fig. 1 Experimental (blue) and calculated (black) central transition ^{115}In NMR spectra of stationary powder samples of (a) $\text{In}(\text{acac})_3$, (b) $\text{In}(\text{trop})_3$, (c) $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_3]_2$ and (d) $\text{Cl}_3\text{In}(\text{TMP})$ acquired at 21.14 T with the quadrupolar-echo pulse sequence.¹¹

Table 1 Experimental ^{115}In NMR parameters^a

	$\text{In}(\text{acac})_3$	$\text{In}(\text{trop})_3$	$\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_3]_2$	$\text{Cl}_3\text{In}(\text{TMP})$
C_Q/MHz	106.0 ± 2.0	160.0 ± 2.0	200.0 ± 4.0	165.0 ± 2.0
η_Q	0.14 ± 0.05	0	0	0.14 ± 0.05
$\delta_{\text{iso}}/\text{ppm}$	-35 ± 10	160 ± 20	-700 ± 40	420 ± 20
δ_{11}/ppm	22 ± 10	280 ± 20	-517 ± 40	470 ± 20
δ_{22}/ppm	-63 ± 10	100 ± 20	-517 ± 40	431 ± 20
δ_{33}/ppm	-63 ± 10	100 ± 20	-1067 ± 40	360 ± 20
Ω/ppm	85 ± 15	180 ± 30	550 ± 60	110 ± 30
κ	-0.90 ± 0.10	-1.00	1.00	0.30 ± 0.10
$\alpha/^\circ$	90 ± 20	90	0	90 ± 15
$\beta/^\circ$	90 ± 5	90	0	0 ± 15
$\gamma/^\circ$	0 ± 5	0	0	0 ± 10

^a $C_Q = eQV_{ZZ}/h$, $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$, where $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$; $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\text{span } \Omega = \delta_{11} - \delta_{33}$, $\text{skew } \kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$, where $\delta_{11} \geq \delta_{22} \geq \delta_{33}$; α , β and γ are Euler angles, the relative orientations of the CS tensors relative to EFG tensors.¹⁵

of non-integer quadrupolar nuclei, quadrupolar-echo¹¹ or quadrupolar Carr–Purcell Meiboom–Gill, QCPMG, sequences¹² in conjunction with stepped-frequency techniques¹³ are employed.

Solid-state ^{115}In NMR results are presented for six-coordinate $\text{In}(\text{acac})_3$ and $\text{In}(\text{trop})_3$, five-coordinate indium(III) triiodide bis(tris(4-methoxyphenyl)phosphine oxide), $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_3]_2$, as well as four-coordinate indium(III) trichloride tris(2,4,6-trimethoxyphenyl)phosphine, $\text{Cl}_3\text{In}(\text{TMP})$. The structures of these complexes in the solid state are sketched

in Scheme 1. The ^{115}In NMR spectra of these samples, acquired at 197.2 MHz using a Bruker Avance II NMR spectrometer operating at 21.14 T, are shown in Fig. 1. ^{115}In QCPMG NMR spectra of stationary samples of $\text{In}(\text{acac})_3$, $\text{In}(\text{trop})_3$ and $\text{Cl}_3\text{In}(\text{TMP})$ were also acquired at 11.75 T, and are provided as ESI.† All spectra were analyzed using the WSolids¹⁴ software to obtain the ^{115}In quadrupolar and chemical shift (CS) parameters as summarized in Table 1.

$\text{In}(\text{acac})_3$ is a tris(β -ketoenolato) complex, with six oxygen atoms positioned in a distorted octahedral arrangement about the central indium atom; each of the three diketo ligands forms a six-membered chelate ring with In.¹⁶ The $\text{In}(\text{acac})_3$ molecules have nearly D_3 symmetry with an approximate C_3 axis perpendicular to the O1–O3–O5 face. The value of $C_Q(^{115}\text{In})$ for solid $\text{In}(\text{acac})_3$, 106.0 ± 2.0 MHz, is in fair agreement with the value of 120 MHz estimated using solution NMR relaxation data which involved several assumptions including $\eta_Q = 0$.¹⁷ The experimental value of η_Q for $\text{In}(\text{acac})_3$ in solid state is actually 0.14 ± 0.05 , indicating that the EFG tensor is indeed close to being axially-symmetric. At the high magnetic-field strengths employed here, the anisotropic magnetic shielding ($\Omega = 85 \pm 15$ ppm) makes a measurable contribution to the line shape. Spectral analysis indicates that the CS tensor is also approximately axially-symmetric and that δ_{11} , the unique component of the CS tensor, is nearly coincident with the largest component of the EFG tensor, V_{ZZ} . Given the local symmetry, we expect V_{ZZ} and δ_{11} to lie along the approximate C_3 axis of the molecule.

The molecular symmetry of $\text{In}(\text{trop})_3$ is D_3 .¹⁸ However, in contrast to $\text{In}(\text{acac})_3$, the tropolonato ions of $\text{In}(\text{trop})_3$ form five-membered chelate rings with In, and the inter-oxygen distances of the “bites” are reduced, which gives rise to a larger EFG at In. As a result, $C_Q(^{115}\text{In})$ for $\text{In}(\text{trop})_3$, 160.0 ± 2.0 MHz, is larger than that observed for $\text{In}(\text{acac})_3$. The isotropic indium chemical shift is also very sensitive to changes in structure, as demonstrated by the deshielding of *ca.* 200 ppm for the indium of $\text{In}(\text{trop})_3$ compared to that of $\text{In}(\text{acac})_3$. The larger span of 180 ± 30 ppm is consistent with the more distorted octahedral arrangement of the oxygen atoms in $\text{In}(\text{trop})_3$. Symmetry requires that the EFG and CS tensors are axially-symmetric. Both V_{ZZ} and δ_{11} are along the C_3 axis of the molecule.

Compared to the distorted octahedral arrangement of the indium center in $\text{In}(\text{acac})_3$ and $\text{In}(\text{trop})_3$, the indium coordination environments in $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_3]_2$ and $\text{Cl}_3\text{In}(\text{TMP})$ are best described as trigonal bipyramidal and tetrahedral respectively.¹⁹ Single-crystal X-ray diffraction data for $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_3]_2$ ¹⁹ indicate that there is one unique In site with D_3 molecular symmetry (see ESI)† with a linear P–O–In–O–P fragment coincident with the C_3 axis. The $C_Q(^{115}\text{In})$ value for this complex, 200.0 ± 4.0 MHz, is the largest found for the four compounds studied here. Also, the indium of this complex is the most shielded and has the largest shielding anisotropy, 550 ± 60 ppm, of the four complexes. The enhanced magnetic shielding of In is caused by the three directly bonded iodine atoms which are known to contribute large relativistic effects.²⁰ The skew, 1.00, indicates that δ_{33} is the unique component of the axially-symmetric CS tensor, thus, V_{ZZ} is coincident with δ_{33} .

Table 2 Calculated ^{115}In NMR parameters

	$\text{In}(\text{acac})_3$	$\text{In}(\text{trop})_3$	$\text{I}_3\text{In}[\text{OP}(\text{CH}_3)_2]_2$	$\text{Cl}_3\text{In}(\text{TMP})$
C_Q/MHz	102.4	164.6	194.1	118.1
η_Q	0.21	0	0	0.17
$\sigma_{\text{iso}}/\text{ppm}$	3875	3628	4752	3394
$\delta_{\text{iso}}/\text{ppm}$	-35 ^a	212	-912	446
δ_{11}/ppm	4	265	-738	473
δ_{22}/ppm	-49	185	-738	453
δ_{33}/ppm	-59	185	-1260	412
Ω/ppm	63	80	522	61
κ	-0.67	-1.00	1.00	0.36
$\alpha/^\circ$	57	90	0	75
$\beta/^\circ$	86	90	0	17
$\gamma/^\circ$	0	0	0	15

^a The calculated value of δ_{iso} for $\text{In}(\text{acac})_3$ was arbitrary set at -35 ppm.

The crystal structure of $\text{Cl}_3\text{In}(\text{TMP})$ ¹⁹ indicates a single unique In site in the unit cell and the presence of an approximate C_3 axis aligned with the In–P bond (see ESI).[†] The $C_Q(^{115}\text{In})$ value is 165.0 ± 2.0 MHz with $\eta_Q = 0.14 \pm 0.05$. The anisotropic magnetic shielding, $\Omega = 110 \pm 30$ ppm, makes a measurable contribution to the line shape at 21.14 T. The EFG tensor is close to axially-symmetric with V_{ZZ} coincident with δ_{33} and aligned along the approximate C_3 axis.

Of the four compounds studied here, the ^{115}In NMR spectrum for $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_2]_2$ was the most challenging to acquire. The breadth of central transition is ca. 1.8 MHz at 21.14 T, so it was acquired in three separate steps, each requiring approximately 11 h. However, it is clear that measurements of $C_Q(^{115}\text{In})$ values in the range of 250–300 MHz are feasible at ultrahigh magnetic-field strengths.

Finally, we have performed ZORA DFT calculations of the EFG and magnetic shielding tensors at indium for compounds $\text{In}(\text{acac})_3$, $\text{In}(\text{trop})_3$ and $\text{Cl}_3\text{In}(\text{TMP})$ (see Table 2 and ESI for details).[†] In the case of $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_2]_2$, it was necessary to substitute $-\text{P}(\text{CH}_3)_3$ for $-\text{P}(p\text{-Anis})_2$ in order to complete the DFT computation in a reasonable time. For all four complexes, the calculated EFG and magnetic shielding tensors are in good agreement with the experimental results. It is particularly gratifying to find that the calculated and observed orientations of the EFG and shielding tensors are in excellent agreement. Also, the large heavy atom effect of iodine on the indium chemical shift is reproduced by the calculations.

In conclusion, we have demonstrated that solid-state ^{115}In NMR studies of representative indium coordination complexes are feasible using high magnetic-field NMR spectrometers. Further ^{115}In NMR studies together with quantum chemistry computations will be required to explore the relationship between ^{115}In NMR parameters and molecular structure.

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- Data of two solved crystal structures (a) $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_2]_2$: $\text{C}_{42}\text{H}_{42}\text{I}_3\text{In}_2\text{O}_8\text{P}_2$, trigonal, $P\bar{3}1c$ (No. 163), $a = 12.9326(4)$ Å, $c = 15.5514(10)$ Å, $V = 2252.53(18)$ Å³, $Z = 2$, $T = 193(2)$ K, $R_1 = 0.0247$ ($wR_2 = 0.0669$) for 1704 observed reflections with $F_0^2 \geq 2\sigma(F_0^2)$; (b) $\text{Cl}_3\text{In}(\text{TMP})$: $\text{C}_{27}\text{H}_{33}\text{Cl}_3\text{In}_2\text{O}_9\text{P}_1$, triclinic, $P\bar{1}$ (No. 2), $a = 10.7470(11)$ Å, $b = 12.3980(13)$ Å, $c = 14.0806(15)$ Å, $\alpha = 93.5129(14)^\circ$, $\beta = 112.0704(12)^\circ$, $\gamma = 108.9252(13)^\circ$, $V = 1608.4(3)$ Å³, $Z = 2$, $T = 193(2)$ K, $R_1 = 0.0285$ ($wR_2 = 0.0801$) for 6840 observed reflections with $F_0^2 \geq 2\sigma(F_0^2)$. Full details are given in the ESI[†].
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