

A solid-state ^{115}In NMR investigation of Indium(III)-Trihalide Phosphine adducts and of octahedral Indium(III) complexes

Roderick Wasylishen, Fu Chen, Guibin Ma, Ronald G. Cavell

University of Alberta, Edmonton, Alberta

roderick.wasylishen@ualberta.ca

Indium coordination complexes find many important applications ranging from materials chemistry to nuclear medicine [1-4]. For example, 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 [1]. The octahedral 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 [2]. The radioactive nuclide, ^{111}In , incorporated in indium(III) tris(tropolonato), $\text{In}(\text{trop})_3$, is commonly used as a labelling agent in diagnostic nuclear medicine [3]. Indium complexes are reasonably well studied in the solution state and are usually characterized by coordination numbers ranging from two to eight [4]. However, structural information for these complexes in the solid state is still relatively scarce.

In this project, we demonstrated that solid-state ^{115}In NMR studies of coordination complexes are feasible, particular at an ultrahigh magnetic-field strength, even though ^{115}In has the largest quadrupole moment, $Q = 81.0 \text{ fm}^2$, of the main group elements. These complexes include 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, $\text{Cl}_3\text{In}(\text{TMP})$ [5]. The ^{115}In NMR spectrum for $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_3]_2$ at 21.1 T is shown in Figure 1.

We extended the study of solid-state ^{115}In NMR to "real" indium coordination complexes such as indium trihalides with triarylphosphine adducts, $\text{X}_3\text{In}(\text{PR}_3)_n$ ($\text{X} = \text{Cl}, \text{Br}$ or I ; $\text{PR}_3 = \text{PPh}_3$, $\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OCH}_3)_3$, $\text{P}(\text{C}_6\text{H}_4\text{-}o\text{-OCH}_3)_3$, $\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-OCH}_3)_3$, $\text{P}[2,6\text{-C}_6\text{H}_3(\text{OCH}_3)_2]_3$ and $\text{P}[2,4,6\text{-C}_6\text{H}_2(\text{OCH}_3)_3]_3$; $n = 1$ or 2) as well as other octahedral compounds such as In_2O_3 . The indium-115 nuclear quadrupolar coupling constants, $C_Q(^{115}\text{In})$ values, and chemical shift, CS, tensors for these compounds were obtained from ^{115}In NMR spectra at both 21.1 and 11.7 T. The effects of both the halide ligands and the indium coordination environment on the indium electric field gradients, EFGs, and CS tensors were systematically studied. For some of these complexes, isotropic

and anisotropic indirect spin-spin coupling values, ${}^1J({}^{115}\text{In}, {}^{31}\text{P})$ and $\Delta J({}^{115}\text{In}, {}^{31}\text{P})$ respectively, were obtained from ${}^{31}\text{P}$ NMR spectra of both stationary and MAS samples. To complement our experimental results, zeroth-order regular approximation density functional theory (ZORA DFT) computations were performed using the Amsterdam Density Functional (ADF) program [6]. The theoretical results are in good agreement with experimental values.

References

- [1] (a) R.L. Wells, S.R. Aubuchon, S.S. Kher and M.S. Lube, *Chem. Mater.* **7** (1995) 793. (b) G.G. Briand, R.J. Davidson and A. Decken, *Inorg. Chem.* **44** (2005) 9914.
- [2] M. Niederberger, *Acc. Chem. Res.* **40** (2007) 793 and references (42), (47) and (48) therein.
- [3] (a) L. Bindslev, M. Haack-Sorensen, K. Bisgaard, L. Kragh, S. Mortensen, B. Hesse, A. Kjaer and J. Kastrop, *Eur. J. Nucl. Med. Mol. Imaging* **33** (2006) 1171. (b) A. Kjaer and A.M. Lebech, *J. Nuc. Med.* **43** (2002) 140.
- [4] (a) D.G. Tuck, In "*Comprehensive Coordination Chemistry*", eds. R.D. Gillard, J.A. McCleverty and G. Wilkinson, Pergamon, Oxford, 1987, vol. 3, 153. (b) A.J. Carty and D.G. Tuck, *Prog. Inorg. Chem.* **19** (1975) 243.
- [5] F. Chen, G. Ma, R.G. Cavell, V.V. Terskikh and R.E. Wasylshen, "Solid-state ${}^{115}\text{In}$ NMR study of indium coordination complexes" *Chem. Commun.* (2008) <http://dx.doi.org/10.1039/b814326a>
- [6] *ADF 2006.01*, Theoretical Chemistry, Vrije Universiteit, Amsterdam.

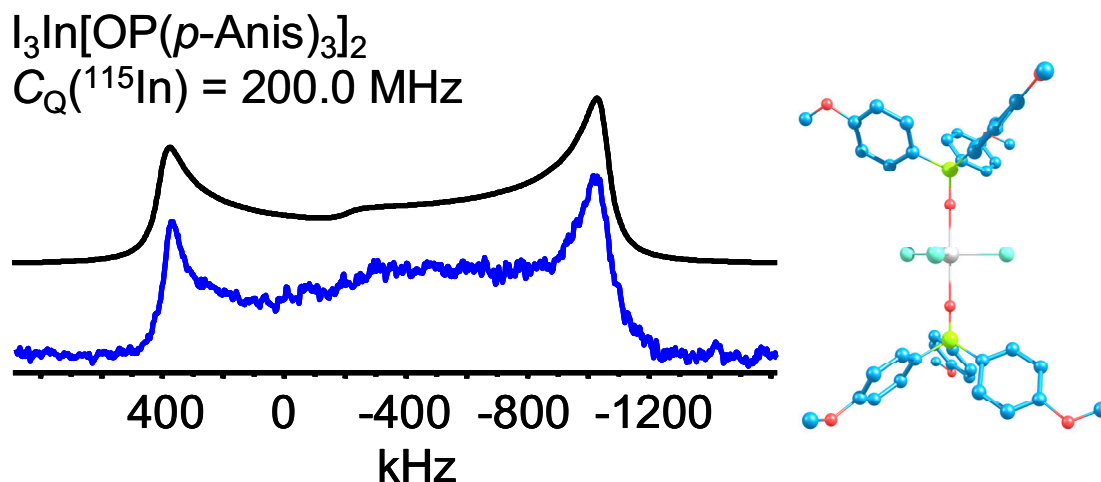


Figure 1: Molecular structure and ${}^{115}\text{In}$ NMR spectrum for stationary $\text{I}_3\text{In}[\text{OP}(p\text{-Anis})_3]_2$ at 21.1 T [5].