

Solid-state NMR studies of colossal framework expansion materials

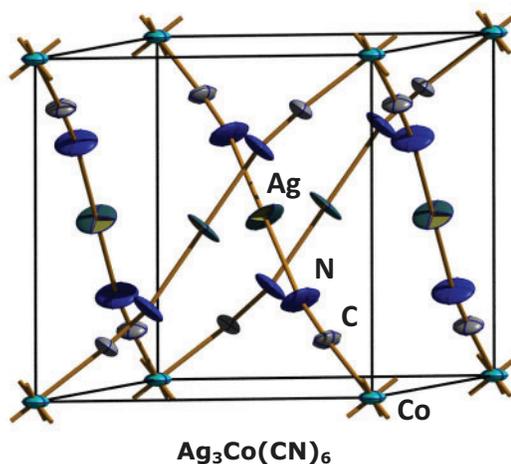
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A major component of our research is the investigation of relationships between molecular structure and NMR parameters. In addition to our investigation of compounds exhibiting colossal thermal expansion, discussed in detail below, recent examples include: the determination of the Ag-P connectivity for some dialkylphosphite salts through the measurement of $J(^{109}\text{Ag}, ^{31}\text{P})$ in solid-state ^{109}Ag and ^{31}P NMR experiments [1]; the relationship between the halide ligands and the ^{115}In magnetic shielding and electric field gradient tensors for a series of X_3InPR_3 adducts ($\text{X} = \text{Cl}, \text{Br}$ or I ; $\text{PR} =$ triarylphosphine ligand) [2]; the use of ^{31}P NMR spectroscopy to characterize some gold phosphide complexes [3] and a ^{13}C NMR investigation of disorder and bonding in gold cyanide complexes [4]. Ongoing projects include a ^{31}P NMR investigation of the spin-spin interactions in complexes with large $C_Q(^{197}\text{Au})$ values, a ^{23}Na NMR study of some sodium salts as well as a ^{31}P and ^{77}Se NMR investigation of diamagnetic and paramagnetic Ni-Se complexes.

Silver hexacyanocobaltate (III), $\text{Ag}_3\text{Co}(\text{CN})_6$ (unit cell pictured), was reported in 2008 to have the largest known combination of positive and negative relative thermal framework expansion [5]. This "colossal" expansion was previously studied by variable-temperature X-ray powder and neutron diffraction techniques. We have investigated the solid-state NMR properties of this compound, primarily focusing



on ^{59}Co NMR [6]. The objective of this research was to examine how the electric field gradient at cobalt and the cobalt magnetic shielding respond to variations in temperature and hence to the large thermal parameters. We found that the ^{59}Co NMR line widths are unusually broad; this is attributed to a distribution of crystal lattice parameters.

We have extended our investigations to other materials that exhibit unusually large thermal expansion coefficients [7, 8]. Following the procedures described by Leznoff and co-workers [7] we have prepared several isostructural silver and gold cyanide polymers that are thought to exhibit metallo-

philic interactions characteristic of heavy closed-shell d^{10} ions, including some indium [7] and zinc [8] dicyanometallates. The crystal structures are trigonal and exhibit positive thermal expansion in their ab planes and negative thermal expansion along their c axes.

Recently, we obtained ^{115}In ($I = 9/2$) NMR data for solid $\text{In}[\text{Au}(\text{CN})_2]_3$ at 11.75 and 21.14 T. The central transition of an ^{115}In NMR spectrum obtained on an 11.75 T instrument has a breadth of less than 150 kHz at room temperature; a fit of this spectrum indicates that $C_Q(^{115}\text{In}) = 36.3 \pm 0.1$ MHz. Because of the relatively small $C_Q(^{115}\text{In})$, it was possible to obtain ^{115}In NMR spectra of MAS samples at 21.14 T with a well-resolved central transition peak. A spectrum of the stationary sample acquired at this field, shown below, is particularly interesting since, besides the well-resolved ^{115}In central-transition observed in this spectrum, the ^{113}In ($I = 9/2$, NA = 4.3 %) central transition is also observed, despite the low natural abundance of the latter. The near unity of the magnetogyric ratios for these nuclei, $\gamma(^{115}\text{In})/\gamma(^{113}\text{In}) = 1.002$, means that the ^{113}In NMR signal appears only 420 kHz to low frequency of that for ^{115}In at 21.14 T.

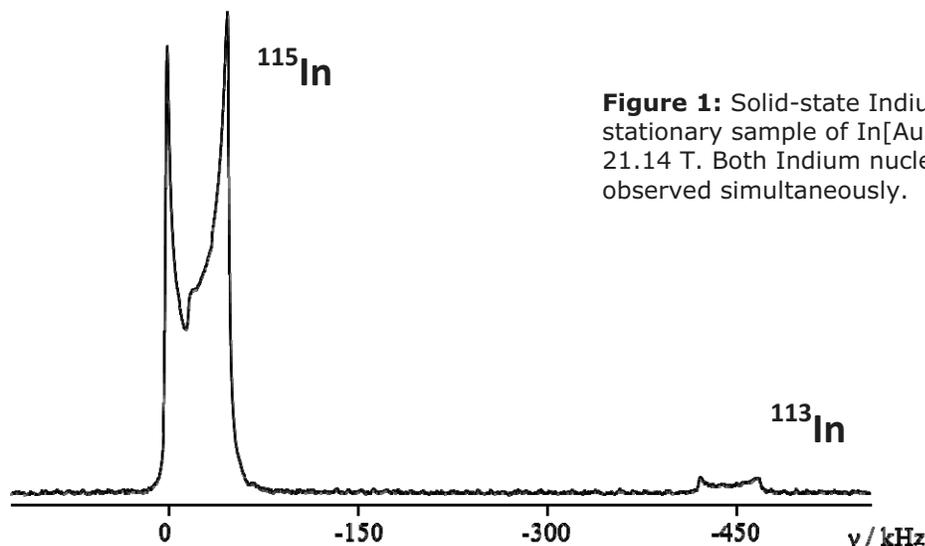


Figure 1: Solid-state Indium NMR spectrum of a stationary sample of $\text{In}[\text{Au}(\text{CN})_2]_3$ recorded at 21.14 T. Both Indium nuclei, ^{113}In and ^{115}In , are observed simultaneously.

References

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