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Ultrahigh-Field Solid-State ^{59}Co NMR Studies of $Co(C_2B_9H_{11})_2^-$ and $Co(C_5H_5)_2^+$ Salts

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The purpose of this contribution is to demonstrate the importance and feasibility of acquiring ultrahigh-field ^{59}Co NMR spectra of solid samples with large nuclear quadrupolar coupling constants, C_Qs. In general, the study of transition metals by NMR spectroscopy has been limited because most of their NMR-active isotopes are quadrupolar.[1−5] The coupling between the nuclear quadrupole moment, Q, and the electric field gradient, EFG, often leads to broad NMR line shapes. Historically, quadrupolar parameters for nuclei at sites with large EFGs could only be determined by nuclear quadrupole resonance, NQR,[6] or single-crystal NMR studies,[7] both of which have significant drawbacks.

Advances in ultrahigh-field magnet technology have allowed an increasing number of NMR-active, non-integer spin quadrupolar nuclei to be investigated by NMR spectroscopy. By acquiring central transition, $m_I = 1/2 \leftrightarrow m_I = -1/2$, NMR spectra of stationary samples, both EFG and chemical shift, CS, tensors can be characterized. When the NMR spectra are extremely broad, stepped-frequency techniques[8−11] are employed, often in conjunction with experiments such as the quadrupolar Carr−Purcell Meiboom−Gill, QCPMG, sequence.[1,12−14] While valuable, QCPMG may not provide the spectral detail necessary to detect subtle effects of the NMR parameters on line shape.[15] Also, to perform QCPMG experiments, the T_2 relaxation time must be long enough to acquire a train of echoes. For powder samples, the most reliable method of characterizing the principal components of the EFG and CS tensors is to simulate the NMR line shapes obtained from single-echo experiments.[16]

Previous studies have demonstrated that ^{59}Co NMR spectra can be acquired when the EFG is relatively small,[4,17−21] but for solid powder samples, the measurement of C_Q values in excess of 100 MHz has not been reported.

Two types of "sandwich" compounds are studied herein: $Co(1,2\text{-}C_2B_9H_{11})_2^-$ and $Co(C_5H_5)_2^+$ salts (see Figure 1). The synthesis and characterization of these compounds have become a fascinating area of research, and many applications of the dicarbollide anion have been discovered, including a recent report that $Co(1,2\text{-}C_2B_9H_{11})_2^-$ and its derivatives act as an inhibitor for HIV protease.[22−24] The $Co(1,2\text{-}C_2B_9H_{11})_2^-$ complex can also adopt different conformations; for example, the relative orientation of the two carboranes can be rotated and are typically either cis, Figure 1, or trans to each other; the Et_3NH^+ and Rb^+ salts adopt the cis conformation.[25,26] There are few NMR studies because the sandwich complexes[27] result in large EFGs at the cobalt. NQR studies have shown that C_Q values range from 138 to 171 MHz,[28] some of the largest reported for ^{59}Co. In solution, large C_Q values result in relaxation times on the order of microseconds, and consequently, large ^{59}Co NMR line widths. In the solid state, large C_Q values result in central transition NMR line shapes with widths on the order of megahertz. Since the second-order quadrupolar interaction scales inversely with the Larmor frequently, it is advantageous to acquire central transition NMR spectra of non-integer quadrupolar nuclei at the highest possible magnetic field strengths.

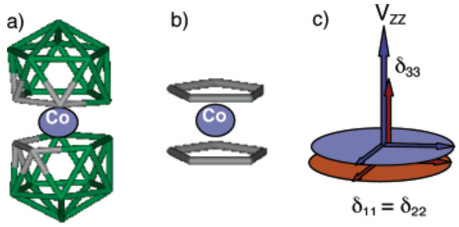

Figure 1. The molecular structure of (a) *cis*-$[Co(1,2\text{-}C_2B_9H_{11})_2]^-$ and (b) $[Co(C_5H_5)_2]^+$; B = green, C = gray; hydrogen atoms have been omitted for clarity. (c) Approximate orientation of the largest component of the ^{59}Co EFG tensors and the principal component of the CS tensor that represents the direction of greatest magnetic shielding in the molecular frame used for (a) and (b).

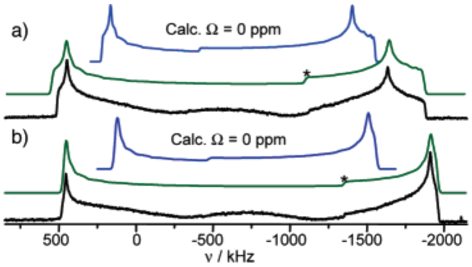

Figure 2. Central transition ^{59}Co NMR spectra of stationary powder samples of (a) $Rb[Co(1,2\text{-}C_2B_9H_{11})_2]$ and (b) $[Co(C_5H_5)_2](PF_6)$ acquired at 21.14 T; (black) experimental, (green) simulated using parameters given in Table 1, (blue) simulated with $\Omega = 0$ ppm. Spectra are referenced to 1.0 M aqueous $K_3Co(CN)_6$ at $\delta = 0$ ppm. The spectra were acquired using three steps of the RF transmitter, 1.0 MHz apart, and combined using the skyline projection technique.[29] Each sub-spectrum was acquired using a pulse delay of 0.5 s.

Cobalt-59 NMR spectra of solid $Co(1,2\text{-}C_2B_9H_{11})_2^-$ salts were acquired at 223.2 MHz using a Bruker Avance 21.14 T NMR spectrometer. Figure 2 shows the ^{59}Co NMR spectrum of $Rb[Co(1,2\text{-}C_2B_9H_{11})_2]$; NMR parameters obtained from the best-fit simulations are presented in Table 1. The central transition spectrum covers approximately 2.5 MHz, representing one of the broadest NMR line shapes observed to date using standard echo experiments. Three different transmitter offsets were used, and each sub-spectrum was acquired in less than 6 h; however, reasonable spectra could be acquired in 1 h. The importance of using ultrahigh magnetic fields is clear; for example, if the spectra were acquired at 11.75 T, the line shapes would be nearly 5 MHz broad and could take days to acquire. Furthermore, the advantage of the single-echo experiment versus QCPMG is demonstrated by the ability to detect the small shoulder in the NMR spectrum near −1.1 MHz, indicated with asterisks in Figure 2. This feature aids in determining both the EFG and CS tensors and would be difficult to observe using a QCPMG experiment.

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Table 1. Experimental ^{59}Co NMR Parameters[a]

	C_Q/MHz (±2)	η_Q (±0.05)	δ_{iso}/ppm (±75)	Ω/ppm (±100)
$RbCo(CB)_2$	163	0.12	−2000	4700
$NaCo(CB)_2$	163	0.08	−2000	4500
$Et_3NH[Co(CB)_2]$	163	0.10	−2000	4600
$[Co(Cp)_2]PF_6$	162	0.02	−2500	5650

[a] CB = $[1,2\text{-}C_2B_9H_{11}]^{-2}$, Cp = $[C_5H_5]^{-1}$; $C_Q = eQV_{ZZ}/h$, $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$, where $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$; $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Omega = \delta_{11} - \delta_{33}$, where $\delta_{11} \geq \delta_{22} \geq \delta_{33}$.[30] Within experimental error, the chemical shift tensors are axially symmetric with the unique component being δ_{33}.

Quadrupolar parameters previously determined using NQR for $Cs[Co(1,2\text{-}C_2B_9H_{11})_2]$, C_Q = 167.76 MHz and η_Q = 0.03,[31] were used as a starting point in the spectral simulations. The best-fit simulation for the Rb^+ salt indicates $C_Q = 163 \pm 2$ MHz and $\eta_Q = 0.12 \pm 0.05$. The noticeable deviation of the EFG tensor from axial symmetry, $\eta_Q \neq 0$, is likely a result of the asymmetry of the $(1,2\text{-}C_2B_9H_{11})^{-2}$ ligands (see Figure 1); X-ray diffraction data obtained for the Cs^+ and Et_3NH^+ complexes indicate that there are no symmetry reasons for the tensors to be axially symmetric.[25,27]

For the axially symmetric cobalt CS tensor, $\delta_{11} = \delta_{22}$, and the span is 4700 ± 100 ppm; $\delta_{iso} = -2000 \pm 100$ ppm. While the lack of rotational symmetry at the Co affects the EFG tensor, the CS tensor remains axially symmetric and appears insensitive to the asymmetry. The relative orientations of the EFG and CS tensors are such that δ_{33} is parallel to V_{ZZ}; see Figure 1c. All three salts of $Co(1,2\text{-}C_2B_9H_{11})_2^-$ studied have similar ^{59}Co NMR spectra and parameters; see Table 1. The ^{59}Co NMR spectrum of $Co(1,2\text{-}C_2B_9H_{11})_2^-$ has not been observed in solution, likely because of the broad peak that results from the expected short spin-relaxation time. However, δ_{iso} for the $Co(1,2\text{-}C_2B_9H_{11})_2^-$ anion was predicted to be −2043 ppm by Bühl, Hynk, and Macháček using computational methods.[32]

The ^{59}Co NMR spectrum of $[Co(C_5H_5)_2](PF_6)$ is also shown in Figure 2.[33,34] The NMR parameters obtained (see Table 1) are in agreement with those previously reported for analogous salts using single-crystal ^{59}Co NMR.[35] The value of C_Q is comparable to those obtained for the $Co(1,2\text{-}C_2B_9H_{11})_2^-$ salts but $\eta_Q = 0$. The CS tensor is also axially symmetric as observed for other cyclopentadienyl sandwich compounds,[36,37] and has a span, $\Omega = 5650 \pm 100$ ppm and $\delta_{iso} = -2500 \pm 100$ ppm. As with the $Co(1,2\text{-}C_2B_9H_{11})_2^-$ salts, δ_{33} is the unique component and is along V_{ZZ}.

The orientation as well as the spans of the cobalt shielding tensors in these two d^6-metal complexes may be rationalized in terms of Ramsey's theory of magnetic shielding using simple molecular theory.[38] Qualitatively, metal-centered MOs of the ground electronic state, which have d_{xy}, $d_{x^2+y^2}$, and d_{z^2} character, overlap with low-lying excited-state MOs that have d_{xz} and d_{yz} character (z is along the molecular pseudo-rotation axis).[39] Efficient mixing of the occupied and unoccupied MOs only occurs when the magnetic field is perpendicular to z, leading to the significant deshielding in this direction, while minimal deshielding occurs when the magnetic field is along z.[40]

In conclusion, we have acquired ^{59}Co NMR spectra of solid $Co(1,2\text{-}C_2B_9H_{11})_2^-$ and $Co(C_5H_5)_2^+$ salts and characterized both the ^{59}Co quadrupolar coupling and CS parameters. The use of ultrahigh magnetic field strengths facilitates the acquisition of ^{59}Co NMR spectra of solids, in a reasonable time, opening up the possibility of using NMR to study a wider range of metal-containing solid materials, metalloenzymes, and biomolecules. Large C_Q values should no longer prevent researchers from performing solid-state ^{59}Co NMR investigations.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Lipton, A. S.; Heck, R. W.; Ellis, P. D. *J. Am. Chem. Soc.* **2004**, *126*, 4735−4739.
(2) Ooms, K. J.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2004**, *126*, 10972−10980.
(3) Pregosin, P. S. *Transition Metal Nuclear Magnetic Resonance*; Elsevier: Amsterdam, 1991.
(4) Chan, J. C. C.; Au-Yeung, S. C. F. *Annu. Rep. NMR Spectrosc.* **2000**, *41*, 1−54.
(5) Mackenzie, K. J. D.; Smith, M. E. *Multinuclear Solid-State NMR of Inorganic Materials*; Pergamon: Oxford, 2002.
(6) Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*; Academic Press: London, 1969.
(7) Eichele, K.; Chan, J. C. C.; Wasylishen, R. E.; Britten, J. F. *J. Phys. Chem. A* **1997**, *101*, 5463−5468.
(8) Nagayama, K.; Bachmann, P.; Wüthrich, K.; Ernst, R. R. *J. Magn. Reson.* **1978**, *31*, 133−148.
(9) Wu, G.; Wong, A.; Wang, S. *Can. J. Chem.* **2003**, *81*, 275−283.
(10) Lipton, A. S.; Wright, T. A.; Bowman, M. K.; Reger, D. L.; Ellis, P. D. *J. Am. Chem. Soc.* **2002**, *124*, 5850−5860.
(11) Schurko, R. W.; Wi, S.; Frydman, L. *J. Phys. Chem. A* **2002**, *106*, 51−62.
(12) Larsen, F. H.; Jakobsen, H. J.; Ellis, P. D.; Nielsen, N. C. *J. Magn. Reson.* **1998**, *131*, 144−147.
(13) Tang, J. A.; Masuda, J. D.; Boyle, T. J.; Schurko, R. W. *Chem. Phys. Chem.* **2006**, *7*, 117−130.
(14) Hamaed, H.; Lo, A. Y. H.; Lee, D. S.; Evans, W. J.; Schurko, R. W. *J. Am. Chem. Soc.* **2006**, *128*, 12638−12639.
(15) Ooms, K. J.; Feindel, K. W.; Terskikh, V. V.; Wasylishen, R. E. *Inorg. Chem.* **2006**, *45*, 8492−8499.
(16) Bodart, P. R.; Amoureux, J.-P.; Dumazy, Y.; Lefort, R. *Mol. Phys.* **2000**, *98*, 1545−1551.
(17) Medek, A.; Frydman, L. *J. Am. Chem. Soc.* **2000**, *122*, 684−691.
(18) Kempgens, P.; Hirschinger, J.; Granger, P.; Rosé, J. *Solid State Nucl. Magn. Reson.* **1997**, *10*, 95−103.
(19) Power, W. P.; Kirby, C. W.; Taylor, N. J. *J. Am. Chem. Soc.* **1998**, *120*, 9428−9434.
(20) Ooms, K. J.; Wasylishen, R. E. *Can. J. Chem.* **2006**, *84*, 300−308.
(21) Lucken, E. A. C.; Noack, K.; Williams, D. F. *J. Chem. Soc A* **1967**, 148−154.
(22) Hawthorne, M. F. *Acc. Chem. Res.* **1968**, *1*, 281−288.
(23) Sivaev, I. B.; Bregadze, V. I. *Collect. Czech. Chem. Commun.* **1999**, *64*, 783−805.
(24) Cígler, P.; Kožíšek, M.; Řezáčová, P.; Brynda, J.; Otwinowski, Z.; Pokorná, J.; Plešek, J.; Grüner, B.; Dolečková-Marešová, L.; Máša, M.; Sedláček, J.; Bodem, J.; Kräusslich, H.-G.; Král, V.; Konvalinka, J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 15394−15399.
(25) Borodinsky, L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 1686−1689.
(26) Based on unpublished single-crystal X-ray diffraction results.
(27) Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1967**, *6*, 1911−1915.
(28) Brill, T. B.; Landon, S. J. *Organometallics* **1982**, *1*, 431−434.
(29) Lipton, A. S.; Wright, T. A.; Bowman, M. K.; Reger, D. L.; Ellis, P. D. *J. Am. Chem. Soc.* **2002**, *124*, 5850−5860.
(30) Mason, J. *Solid State Nucl. Magn. Reson.* **1993**, *2*, 285−288.
(31) Harris, C. B. *Inorg. Chem.* **1968**, *7*, 1517−1521.
(32) Bühl, M.; Hnyk, D.; Macháček, J. *Chem.*—*Eur. J.* **2005**, *11*, 4109−4120.
(33) Braga, D.; Scaccianoce, L.; Grepioni, F.; Draper, S. M. *Organometallics* **1996**, *15*, 4675−4677.
(34) The two crystallographically unique Co sites in $[Co(C_5H_5)_2](PF_6)$ could not be distinguished in the ^{59}Co NMR spectrum.
(35) Spiess, H. W.; Haas, H.; Hartmann, H. *J. Chem. Phys.* **1969**, *50*, 3057−3064.
(36) Willans, M. J.; Schurko, R. W. *J. Phys. Chem. B* **2003**, *107*, 5144−5161.
(37) Schurko, R. W.; Hung, I.; Macdonald, C. L. B.; Cowley, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 13204−13214.
(38) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699−703.
(39) Evans, S.; Green, M. L. H.; Jewitt, B.; King, G. H.; Orchard, A. F. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 356−376.
(40) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, *40*, 1714−1724.

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