Anisotropic Nuclear Spin Interactions in K₂Hg(CN)₄: A Multinuclear Solid-State NMR Study

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Several anisotropic nuclear spin interactions in solid potassium tetracyanomercurate(II), K₂Hg(CN)₄, have been characterized using ¹³C, ¹⁵N, and ¹⁹⁹Hg NMR spectroscopy at 4.70 and 9.40 T. The carbon chemical shielding tensor is axially symmetric, with anisotropy, Δσ = σ₁ - σ₃ = 329 ± 2 ppm. From the ¹³C and ¹⁹⁹Hg NMR spectra obtained with magic-angle spinning (MAS), Ω(¹⁹⁹Hg, ¹³C)ₙ₁₀ = 1540 ± 2 Hz; analysis of the ¹⁹⁹Hg NMR spectra of a static powder sample indicates that this indirect spin–spin interaction is anisotropic, ΔΩ(¹⁹⁹Hg, ¹³C) = 950 ± 60 Hz. The first report of Ω(¹⁹⁹Hg, ¹⁴N) in the solid state is obtained from an analysis of ¹⁹⁹Hg MAS NMR spectra; Ω(¹⁹⁹Hg, ¹⁴N)ₙ₀ = 20.6 ± 2.0 Hz and Ω(¹⁹⁹Hg, ¹⁵N)ₙ₀ = 29.0 ± 2.0 Hz. The effective dipolar coupling between ¹⁹⁹Hg and ¹⁴N nuclei, Rₑffective = 20.0 Hz, is found to be significantly smaller than the direct dipolar interaction, Rₐ = 43.0 Hz. This reduction is attributed to anisotropy in the indirect spin–spin coupling; Ω(¹⁹⁹Hg, ¹⁴N) = 69 ± 15 Hz. Analysis of ¹⁴N NMR spectra obtained with slow MAS indicates that the nitrogen chemical shift tensor is axially symmetric, with an anisotropy of 477 ± 5 ppm.

Introduction

Solid-state NMR techniques provide experimentalists with an opportunity to characterize the orientation dependence of various NMR parameters. For example, the analysis of the NMR line shape resulting from an isolated spin ½ nucleus in a static powder sample allows one to measure the three principal components of the chemical shift tensor. If the spin ½ nucleus is coupled to an adjacent spin, one can, in principle, also obtain information about the direct dipole–dipole coupling and the indirect, electron-mediated spin–spin (J) coupling tensors. While information concerning the orientation dependence of carbon and nitrogen chemical shift tensors is available for most important functional groups in numerous compounds, much less is known about the anisotropy of indirect spin–spin tensors involving these nuclei. Recently, it has been demonstrated that several one-bond indirect spin–spin couplings involving mercury and phosphorus and platinum and phosphorus are anisotropic. The implication is that mechanisms other than the commonly accepted Fermi-contact mechanism must be important for these couplings.

One of the primary objectives of the present study was to determine whether or not J(¹⁹⁹Hg, ¹³C) is anisotropic. Solid K₂Hg(CN)₄ is an ideal compound to investigate for this purpose since diffraction studies indicate that the crystals are cubic; the space group is Fd₃m. This places the mercury at the center of the symmetric Hg(CN)₂⁻ tetrahedron. The site symmetry at mercury makes solid-state ¹⁹⁹Hg NMR studies feasible since the ¹⁹⁹Hg chemical shift anisotropy must be zero for T₃ symmetry. As well, the J tensors involving mercury must be axially symmetric; this also simplifies the spectral analysis and the interpretation of the results. Furthermore, extensive ¹⁴N nuclear quadrupole resonance (NQR) studies of K₂Hg(CN)₄ have been carried out providing information about the ¹⁴N nuclear quadrupole coupling constant. This information is important in the analysis of ¹⁹⁹Hg NMR line shapes obtained in magic-angle spinning (MAS) experiments. In the course of this study we also determined the orientation dependence of the ¹³C and ¹⁵N chemical shifts in K₂Hg(CN)₄. As well, we became aware of a number of subtleties associated with analyzing MAS spectra of spin ½ nuclei that are coupled to quadrupole nuclei. Since many of these have been neglected or misinterpreted in the past, we discuss them in some detail. Before presenting the results of our study, a brief review of the background theory is provided.

Theoretical Background

To describe the NMR spectrum of a spin ½ nucleus (e.g., ¹³C, ¹⁵N, ¹⁹⁹Hg) in a solid powder sample made up of a collection of crystallites, one must consider the orientation dependence of several nuclear spin interactions. First, the chemical shielding experienced by a particular nucleus in any given crystallite will depend on the orientation of that crystallite in the applied magnetic field, B₀. Second, the spin ½ nucleus under observation (the I spin) may be spin–spin coupled to a neighboring nucleus, S, via two different interactions, a direct dipole–dipole interaction and an indirect electron mediated spin–spin interaction. The direct dipolar interaction depends on the inverse cube of the internuclear separation, R⁻³, and on the orientation of the internuclear vector in B₀. Although indirect spin–spin coupling constants, J(I,S), are often assumed to be scalars (isotropic), they too, in principle, may be anisotropic.

In the case of the tetrahedral Hg(CN)₂⁻ ion all nuclei lie along C₃ axes. Under these conditions the carbon and the nitrogen chemical shift tensors are axially symmetric as are the indirect spin–spin interactions. For such a spin pair, the resonance frequency of the I spin is given by the equation

\[ v_{mI}(\theta) = v_L - v_{CS} - m_Sv_D - m_SJ_{iso} \]  

where

\[ v_L = \gamma I B_0 / 2\pi \]  

\[ v_{CS} = \gamma I B_0 \left[ \sigma_{iso} - \Delta\sigma / 3 \right] \]  

\[ v_D = R_{effective} (1 - 3 \cos^2 \theta) \]

and J_{iso} is the isotropic value of the indirect spin–spin coupling tensor. In these expressions θ is the angle between any given C₃ symmetry axis and B₀, σ_{iso} is the isotropic value of the chemical shielding tensor, Δσ is the chemical shielding anisotropy, and R_{effective} is the effective dipolar coupling constant. These parameters are defined in eqs 2–4.

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\[ \sigma_{\text{iso}} = \left(2\sigma_\perp + \sigma_\parallel\right)/3 \]

\[ \Delta \sigma = \sigma_\parallel - \sigma_\perp \]

\[ R_{\text{eff}} = R_{\text{DD}} - \Delta J/3 \]

where the direct dipolar coupling constant, \( R_{\text{DD}} \), is \((\mu_0/4\pi)(\gamma_1\gamma_2/2\pi)(r_1r_2^{-3})\) and the anisotropy in the indirect spin-spin coupling is defined as \( \Delta J = J_\parallel - J_\perp \). The total spin 1/2 NMR powder line shape is obtained by considering all possible angles \( \theta \). Each of the 2S + 1 transitions \((m_S = -S, -S + 1, ..., S - 1, S)\) must be added to give the total I-spin powder spectrum.

Equation 1 is only strictly valid for cases where both \( I \) and \( S \) spins are spin 1/2 nuclei. If the \( S \) spin is quadrupolar (e.g., \(^{14}\text{N}\), \( S = 1 \)), the pure Zeeman states of the quadrupolar nucleus, \((S,m_S)\), may not be eigenstates of the total Hamiltonian. However, provided the ratio of the quadrupolar to Zeeman energies is small, Olivieri and co-workers\(^{11,12}\) have presented a simple first-order perturbation approach which is useful for calculating eigenstates of quadrupolar nuclei. For the \( \text{Hg}(CN)_2^{2-} \) ion, \(^{14}\text{N} \) chemical shifts are referenced with respect to liquid ammonia.\(^{13}\)

Nitrogen-15 chemical shifts were also prepared by this procedure, except that a 3:1 mixture of \(^{14}\text{N} \) and \(^{15}\text{N} \) were recorded at 4.70 T on a Bruker MSL 200 spectrometer, respectively. A typical sample spinning frequency in the range 2.0-4.0 kHz. Nitrogen-15 chemical shifts are sensitive to the breakdown of the high-field approximation, and Olivieri's first-order perturbation approach\(^{11,12}\) must be implemented. This approach will be used to calculate the spin 1/2 MAS line shapes exhibited by the \(^{13}\text{C}-^{14}\text{N} \) and \(^{199}\text{Hg}-^{14}\text{N} \) spin pairs of \( \text{Hg}(CN)_2 \).\(^{14}\)

Experimental Section

Crystalline samples of \( \text{K}_2\text{Hg}(CN)_4 \) were prepared by dissolving 0.020 mol of KCN and 0.010 mol of \( \text{Hg}(CN)_2 \) in methanol and then evaporating the solvent. A partially \(^{13}\text{C} \) enriched sample was also prepared by this procedure, except that a 3:1 mixture of KCN and \(^{13}\text{C} \) labeled \( \text{K}_2\text{Hg}(CN)_4 \) precipitated from an aqueous solution of \( \text{K}_2\text{Hg}(CN)_4 \) with that of \( \text{Hg}(CH_3)_2 \), which is 17.910 841 MHz in a magnetic field such that the protons of TMS resonate at exactly 100.0 MHz.\(^{15}\)

Mercury-199 chemical shifts were referenced to \( \text{Hg}(CH_3)_2 \) by comparing the observed \(^{199}\text{Hg} \) NMR frequency of solid \( \text{K}_2\text{Hg}(CN)_4 \) with that of \( \text{Hg}(CH_3)_2 \), which is 17.910 841 MHz in such a magnetic field such that the protons of TMS resonate at exactly 100.0 MHz.\(^{15}\)

The \(^{13}\text{C} \) isotropic MAS NMR powder spectrum\(^{16}\) was obtained by adding the intensities of all the spinning sidebands in the \(^{13}\text{C} \) MAS NMR spectrum. Carbon-13 MAS NMR spectra were calculated using the first-order perturbation method of Olivieri,\(^{11,12}\) incorporating the POWDER routine of Alderman, Solum, and Grant.\(^{16}\) Simulations of \(^{199}\text{Hg} \) static and MAS NMR spectra were based on a FORTRAN program developed in this laboratory.

Results and Discussion

Carbon-13 MAS NMR Spectra. A typical \(^{13}\text{C} \) MAS NMR spectrum of \( \text{K}_2\text{Hg}(CN)_4 \) is shown in Figure 1, where the sample spinning rate was 2945 Hz. The isotropic region consists of three asymmetric doublets: the central intense asymmetric doublet is due to \(^{13}\text{C} \) nuclei attached to magnetically inactive mercury nuclei while the doublets which flank the central doublet are due to \(^{13}\text{C} \) nuclei bonded to \(^{199}\text{Hg} \) \((I = 1/2, \text{natural abundance} = 16.84\%)\). From separations involving the outer doublets, \( J(\text{Hg}-\text{C})_{199\text{Hg}} = 1540 \pm 2 \text{ Hz} \). This coupling constant is much smaller than that found in \( \text{Hg}(CN)_2 \), 3158 Hz.\(^{11,16}\) This observation is in agreement with qualitative arguments based on the "s-character" of the mercury–carbon bond;\(^{16}\) however, such simple arguments must be treated with caution (vide infra). Although splittings due to \(^{31}\text{P}, 201\text{Hg} \) couplings (201\text{Hg}, \( I = 3/2, \text{natural abundance} = 13.22\% \)) have been recently observed in \(^{13}\text{C} \) MAS NMR spectra of mercury phosphine complexes,\(^{19,20}\) no splittings due to \(^{13}\text{C} \) and \(^{201}\text{Hg} \) coupling were observed in the \(^{13}\text{C} \) MAS NMR spectra of \( \text{K}_2\text{Hg}(CN)_4 \). The absence of \( 201\text{Hg} \) satellite peaks is attributed to rapid \( 201\text{Hg} \) spin–lattice relaxation (\( T(201\text{Hg}) < 1 \text{ ms} \)) which results in self-decoupling. The rapid \( 201\text{Hg} \) relaxation is a consequence of the large \( 201\text{Hg} \) nuclear quadrupole moment interacting with fluctuating electric field gradients which are induced by lattice vibrations and librational motions of the \( \text{Hg}(CN)_2 \) tetrahedra.

Whenever a \(^{13}\text{C} \) nucleus is directly bonded to \(^{14}\text{N} \) \((I = 1, \text{natural abundance} = 99.63\%)\), the high-resolution \(^{13}\text{C} \) MAS NMR line shape of that particular carbon is generally an asymmetric doublet.\(^{12,23,24}\) This doublet arises from the fact that the \(^{13}\text{C}–^{14}\text{N} \) direct dipolar interaction is not averaged to zero by MAS because the \(^{14}\text{N} \) nuclei are not completely quantized by the applied magnetic field (i.e., \( |\langle \gamma(14N)\rangle|/\langle(14N)\rangle \geq 0 \)). Several theoretical treatments of this problem have been developed. Among them, a simple approach based on first-order perturbation theory has been shown to be convenient.\(^{11,12}\) However, all theoretical treatments of this problem are based on the assumption that the \(^{13}\text{C} \) chemical shift anisotropy (CSA) is negligible or that the fast-spinning limit is satisfied. It has been previously noticed.

![Figure 1. \(^{13}\text{C} \) MAS NMR spectrum of \( \text{K}_2\text{Hg}(CN)_4 \) at 4.70 T. The spinning frequency was 2945 Hz. The isotropic region together with spinning sidebands is shown. The order of the sidebands to high frequency of the isotropic peaks is indicated by positive integers.](image-url)
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where it was assumed that the unique components of the spin ½ chemical shift and spin 1 EFG tensors were coincident. Clearly, this assumption is valid for K₂Hg(CN)₄ where both the carbon chemical shift and nitrogen EFG tensors are axially symmetric with the unique component lying along the linear Hg–C–N bonding axis.

As mentioned above, when a large number of spinning sidebands exist, the isotropic part of the MAS NMR spectrum cannot be reproduced by previous NMR line shape calculations. Since those line shape calculations are based on averaging over one rotor period, they should be associated with the "isotropic MAS NMR powder spectrum", a spectrum obtained by synchronous acquisition. When spinning sidebands are present, it is the sum of all spinning sidebands, rather than the center band, which represents the "isotropic MAS NMR powder spectrum". Therefore, one must compare the sum of all spinning sidebands with the line shape calculated by previous methods such as that based on perturbation theory. This is clearly illustrated in Figure 2. While the different order spinning sidebands vary markedly, the sum of all spinning sidebands (Figure 2d) compares well with the MAS line shape calculated using Olivieri's approach.

In a recent ¹³C solid-state NMR study of [(n-C₃H₇)₄]-N][Cd(SCN)₃], the first measurement of ¹³C,¹⁴N in a solid sample was reported. In the ¹³C MAS NMR spectrum of K₂Hg(CN)₄, no splitting due to ¹³C,¹⁴N was observed at the high-frequency region of the asymmetry tensor, indicating that the coupling is small. In fact, ¹³C,¹⁴N is expected to be approximately 5.1 Hz, based on a solution NMR study, in which a value of 7.2 Hz was reported for ¹³C,¹⁴N in Hg(CN)₂⁻.

The isotropic ¹³C chemical shift of K₂Hg(CN)₄ is approximately 262.8 ppm, and ²⁻ 66.3 ppm. The chemical shift anisotropy, is dipolar coupled to a ¹⁴N nucleus and the high-field approximation is not strictly valid for the quadrupolar nucleus. They found that the calculated MAS line shapes differ for the different order spinning sidebands. Here we present an experimental example which clearly demonstrates that the MAS line shape changes dramatically for the different order spinning sidebands as predicted by theory.

For K₂Hg(CN)₄, the carbon chemical shift anisotropy is quite large (Δν = 15 kHz at B₀ = 4.70 T), and the presence of several spinning sidebands is inevitable at normal spinning rates (see Figure 1). In Figure 2, several of the spinning sidebands are shown on an expanded scale for easy comparison. It is obvious that the MAS line shapes vary for the different order spinning sidebands. The detailed ¹³C MAS NMR line shapes observed for solid K₂Hg(CN)₄ resemble those calculated by Sethi et al.,

Figure 2. (a) ± 1, (b) 0, and (c) ± 2 order spinning sidebands, and (d) the sum of all spinning sidebands in the ¹³C MAS NMR spectrum of K₂Hg(CN)₄. (e) Calculated ¹³C NMR spectrum using R(¹³C,¹⁴N) = 1.29 kHz, α(¹⁴N) = -40 MHz, α(¹³C) = 14.4 MHz, and ¹³C,¹⁴N = 5.1 Hz. Note that the plus sign indicates a high-frequency spinning sideband.

Recently, Sethi et al. have shown that it is possible to calculate the detailed spin ½ NMR line shapes of the isotropic and MAS sideband peaks under conditions where the spin ½ nucleus is dipolar coupled to a spin 1 nucleus and the high-field approximation is not strictly valid for the quadrupolar nucleus. They found that the calculated MAS line shapes differ for the different order spinning sidebands. Here we present an experimental example which clearly demonstrates that the MAS line shape changes dramatically for the different order spinning sidebands as predicted by theory.

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The 199Hg NMR spectrum of a partially 13C enriched powder sample of solid K₂Hg(CN)₄.

Analysis of the static ¹³C NMR spectrum of K₂Hg(CN)₄ yields an effective ¹³C-¹⁴N dipolar coupling constant of 1.29 kHz, which implies a C-N bond length of 1.19 Å assuming ΔJ(¹³C,¹⁴N) = 0. The bond distance derived from the analysis of the ¹³C NMR static spectrum is somewhat longer than that obtained from the neutron diffraction study; 1.16 Å. As is well-known, the dipolar coupling constant measured in NMR experiments is an effective value, R_eff. It is clear from eq 4 that any derivation of internuclear distances from the observed R_eff is based on two assumptions: (1) anisotropy in the J tensor is negligible, and (2) motional averaging is negligible. Since J(¹³C,¹⁴N) is only 5.1 Hz, ΔJ(¹³C,¹⁴N) is expected to be negligible; thus, the smaller value of R_eff observed compared with that calculated using R_CN = 1.16 Å (R_DD = 1.399 kHz) must be attributed to motional averaging of the direct dipolar interaction. Based on the calculated value of R_DD and the observed value of R_eff, the reduction of the direct ¹⁴N, ¹³C dipolar coupling constant due to motional averaging of the CN vector is approximately 8%.

Analysis of the ¹⁹⁹Hg NMR Spectra of a Static Powder Sample. The ¹⁹⁹Hg NMR spectrum of a partially ¹³C enriched powder sample of K₂Hg(CN)₄ consists of a central peak and two satellites; see Figure 3a. The separation between the two satellites, 1540 Hz, confirms the value of ΔJ(¹⁹⁹Hg,¹³C)obs which was obtained from the ¹³C MAS NMR spectrum. The full width at half-height of the central peak, 218 Hz, is essentially independent of the applied magnetic field, providing further evidence that the site symmetry at mercury is T₉ and that the ¹⁹⁹Hg chemical shift tensor is isotropic. The line width of the central peak is mainly due to the dipolar and J interactions with four adjacent ¹⁴N nuclei in the molecule (vide infra). The ¹⁹⁹Hg chemical shift of solid K₂Hg(CN)₄ is -463 ppm with respect to Hg(CH₃)₂.

It is readily seen from Figure 3 that the line widths of the ¹³C satellites are approximately the same as that of the central ¹⁹⁹Hg NMR peak. Analysis of the static line shape yields the effective dipolar coupling constant between ¹⁹⁹Hg and ¹³C nuclei, R_eff(¹⁹⁹Hg,¹³C)eff = 225 ± 20 Hz. Note that the ¹⁹⁹Hg NMR line shapes of the ¹³C satellites depend on the relative sign of J(¹⁹⁹Hg,¹³C) and R_eff(¹⁹⁹Hg,¹³C)eff. Since the sign of J(¹⁹⁹Hg,¹³C) in several organomercury compounds is known to be positive, our analysis indicates that R_eff(¹⁹⁹Hg,¹³C)eff is positive. The ¹⁹⁹Hg NMR spectrum obtained at 9.40 T was very similar to the spectrum obtained at 4.70 T except that the half-height line width, 288 Hz, was slightly larger than the value at 4.70 T, 218 Hz. The value of R_eff, 225 Hz, was also confirmed by fitting the ¹⁹⁹Hg NMR spectrum obtained at 9.40 T. Based on the Hg-C bond length of 2.152 Å from diffraction studies, the calculated direct dipolar coupling constant, R_DD, is 542 Hz. Thus, R_eff is approximately 60% less than R_DD. Since motional averaging in solid K₂Hg(CN)₄ only results in an 8% reduction in R_DD(¹³C), the larger reduction of R_eff(¹⁹⁹Hg,¹³C) compared to R_DD(¹⁹⁹Hg,¹³C) cannot be attributed to motional averaging. Since R_eff has the same sign as R_DD, ΔJ(¹⁹⁹Hg,¹³C) is estimated to be 950 ± 60 GHz.

Figure 3. Experimental (a) and calculated (b) ¹⁹⁹Hg NMR spectra of a static, partially ¹³C enriched powder sample of solid K₂Hg(CN)₄.

Hz. This value compares well with that obtained for Hg(CH₃)₂ in a liquid crystal solvent, ΔJ(¹⁹⁹Hg,¹³C) = 864 Hz. Since ΔJ(¹⁹⁹Hg,¹³C) in K₂Hg(CN)₄ can be assumed positive, 4J₁ = 2170 ± 60 Hz and J₁ = 1220 ± 60 Hz, indicating that a stronger electron-nucleus interaction exists when the magnetic field lies parallel to the Hg-C bond as opposed to being perpendicular. Previously, it has been found that J₁ > J₉ for several other indirect spin-spin coupling tensors such as J(¹⁹⁹Hg,¹³C), J(¹⁹⁵Pt,³¹P), J(¹⁹⁵Pt,³¹P), and J(¹⁶⁵Cu,³¹P). Analysis of ¹⁹⁹Hg MAS NMR spectra. The ¹⁹⁹Hg MAS NMR spectra of solid K₂Hg(CN)₄ at 4.70 and 9.40 T are shown in Figure 4. Compared with the ¹⁹⁹Hg NMR spectrum of a static sample, shown in Figure 3, the line width is reduced to about 100 Hz, and some splittings are clearly visible.

As discussed above, an asymmetrical doublet is generally observed in the MAS NMR spectra of spin 1/2 nuclei that are dipolar coupled to a spin 1 nucleus such as ¹⁴N. If the J coupling between these two nuclei is large enough to be resolved, a triplet pattern with nonequal spacing results. The two separations within the triplet can be written as

\[ |J| \omega + 3d \quad \text{and} \quad |J| \omega - 3d \]  

Here, \( d \) is defined as

\[ d = - \frac{3}{10} \frac{R_{eff} \chi}{V_{L}(S)} \]  

where R_eff is the effective dipolar coupling constant between the spin 1/2 and spin 1 nuclei, \( \chi \) is the quadrupolar coupling constant of the spin 1 nuclei, and \( V_{L}(S) \) is the Larmor frequency of the spin 1 nuclei. It should be noted that eq 6 is valid only for an axially symmetric EFG tensor at the spin 1 nucleus with the unique component lying along the internuclear vector, as is the case in K₂Hg(CN)₄. More general expressions can be found elsewhere.

Since the ¹⁹⁹Hg nucleus is adjacent to four equivalent ¹⁴N nuclei in K₂Hg(CN)₄, the resultant multiplet is rather complicated; however, one can still analyze these spectra. In Figure 4 the calculated stick spectra and the spectra convoluted with a Gaussian function of 1.6 Hz are shown. The best fit of the ¹⁹⁹Hg MAS spectra yields \( |J| \omega(¹⁹⁹Hg,¹⁴N) = 20.6 ± 2.0 \) Hz; \( d = 1.65 ± 0.4 \) and 0.82 ± 0.4 Hz at 4.70 and 9.40 T, respectively. It is known that the resultant pattern is independent of the signs of J₁, J₀, and R_eff but is sensitive to the sign of \( \chi \). The positive sign obtained for \( d \) indicates that \( \chi(¹⁴N) \) is negative. Negative values for \( \chi(¹⁴N) \) have been reported for other compounds containing the cyano group.
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Figure 5. Calculated ¹⁹¹Hg MAS NMR spectra as a function of d: (a) 1.20, (b) 1.60, (c) 2.00, (d) 2.40, and (e) 2.80 Hz. In all cases, $|\langle J^{(199,14N)} \rangle| = 20.6 \text{ Hz}$.

Based on the Hg–N separation obtained from the neutron diffraction study, 3.312 Å, and the ¹⁴N quadrupole coupling constant, −4.047 MHz, obtained from NQR measurements, the calculated value of d is significantly larger than the observed value of 1.65 Hz. Similar discrepancies are also evident from the data at 9.40 T where the calculated and observed values are 1.78 and 0.82 Hz, respectively. From the value of d, the effective dipolar coupling constant, $R_{DD}$, is determined to be 20.0 Hz, which is significantly smaller than the calculated value for the direct dipolar coupling between ¹⁹¹Hg and ¹⁴N nuclei, $R_{DD} = 43.0 \text{ Hz}$. It should be emphasized that the MAS multiplet simulation is sensitive to small variations in d. To illustrate the sensitivity of the ¹⁹¹Hg MAS multiplet to d, several calculated spectra are shown in Figure 5, in which d varies from 1.20 to 2.80 Hz in steps of 0.40 Hz. Clearly a change in d, even as small as 0.40 Hz, can cause noticeable variation in the ¹⁹¹Hg MAS multiplet. This can be rationalized by noting that any change in d is first amplified by a factor of 3 (see eq 5) and then further enhanced by a factor of 4 because of the presence of four equivalent ¹⁴N nuclei.

As we have already established from our analysis of the static ¹⁹¹Hg NMR spectrum of ¹³C labeled K₂Hg(CN)₄, the small value of $R^{(199,13C)}_{(eff)}$ relative to $R^{(199,13C)}_{DD}$ implies that $\Delta J^{(199,13C)}$ is nonzero. Similarly, the observation of a significantly smaller $R_{eff}$ between ¹⁹¹Hg and ¹⁴N nuclei suggests that $\chi^{(199,14N)}$ is also anisotropic. Several other possible factors that could be responsible for the reduction in $R^{(199,14N)}_{(eff)}$ were considered.

Motional Averaging. Because ¹⁹¹Hg is at the center of the Hg(CN)₄ tetrahedron and is relatively far from the terminal nitrogen atoms, $R_{DD}$ is not very sensitive to the motional averaging of the cyano group. This can be appreciated if one considers a plot of $R_{DD}$ as a function of internuclear separation. Since $R_{DD} \propto 1/r^3$, the sensitivity of $R_{DD}$ to variations in r is attenuated at long internuclear separations. At r = 3.312 Å, a displacement of 0.20 Å, which is unreasonably large, causes only an 18% reduction in $R_{DD}$. As we have indicated above, the C–N separation derived from our ¹³C NMR study, which is a measure of a motionally averaged C–N distance, differs from the neutron diffraction result by only 0.03 Å. The neutron diffraction study of K₂Hg(CN)₄ indicated that the crystal structure is relatively independent of temperature, suggesting rather rigid Hg(CN)₄ tetrahedra.

An inelastic neutron scattering study has shown that librational motion (rotation) of the Hg(CN)₄ about [111] is associated with the observed phase transition at 111 K. However, this motion cannot provide an explanation for the observed reduction of d, because (a) the librational amplitude is small (~2.5° at 298 K) and (b) this librational motion would also affect the ¹³C–¹⁴N dipolar coupling.

Validity of Eqs 5 and 6. Since eqs 5 and 6 are based on a first-order perturbation approach, it is important to estimate corrections due to higher-order perturbation terms. As is known, second-order perturbation terms do not affect isotropic positions of the MAS line shapes and so is constant to $(x_1/x_2)^2$. In the present case, the ratio $x_1/x_2$ equals 0.28 and 0.14 at 4.70 and 9.40 T, respectively. Therefore, higher-order corrections to d will be less than 2%. If high-order terms were operative, one would expect a better fit for the spectrum obtained at the higher field, 9.40 T. In contrast, we are able to reproduce both spectra using the same set of parameters, indicating that high-order terms are indeed negligible.

It then seems impossible to rationalize the observed reduction in d without introducing a sizable anisotropy in $J^{(199,14N)}$. Based on the calculated and observed d values, $\Delta J^{(199,14N)} = 69 \pm 15 \text{ Hz}$, assuming that $R_{eff}$ has the same sign as $R_{DD}$. The error of ±15 Hz was estimated assuming that the uncertainty in d is 0.4 Hz. From the ratio of $\gamma^{(199,14N)}/\gamma^{(14N)}$, $\Delta J^{(199,14N)}$ is expected to be $-97 \pm 20 \text{ Hz}$. Since the magnitude of $\Delta J^{(13C,15N)}$ is greater than the corresponding isotropic value, $J^{(199,14N)}_{iso}$, it is possible that $\Delta J$ and $\Delta J$ may have opposite signs. To date, there have been few reports of $\Delta J$ in the literature. For acetonitrile, Diehl et al. reported $\Delta J^{(13C,15N)} = -16 \text{ Hz}$. In a more recent and extensive study of acetonitrile in several liquid crystal solvents, a value of −18 Hz was obtained for $\Delta J^{(13C,15N)}$. This value can be compared with the results of a molecular orbital calculation, −8 Hz. Although the agreement is only qualitative, it is probably significant that the calculations indicated that the anisotropy in $J^{(13C,15N)}$ is dominated by the cross term between the Fermi contact and spin–dipolar interactions. Since reliable MO calculations involving heavy atoms such as mercury are still difficult, a complete understanding of indirect spin–spin interaction requires much more effort from both theoreticians and experimentalists. Nevertheless, the large anisotropy observed in $J^{(199,14,12N)}$ implies that non-Fermi contact terms are important in transmitting nuclear spin information via electrons. In two recent solid-state NMR studies, $\Delta J$ values have been reported in phosphine–copper(I) complexes and hexachloroplatinates by analyzing quadrupole-perturbed MAS spectra of ³¹P and ¹⁹¹Pt nuclei, respectively.

Mercury-199 MAS experiments were also carried out on a 70% ¹⁴N enriched sample of K₂Hg(CN)₄ at 4.70 T; a typical spectrum is shown in Figure 6a. For this particular sample it is easy to show that the probability of a ¹⁹¹Hg nucleus being bonded to four, three, two, one, and zero ¹⁴N groups is 0.2401, 0.4116, 0.2646, 0.0756, and 0.0081, respectively. The ¹⁹¹Hg MAS line shape has been calculated using these relative populations (see Figure 6b). The parameters used to calculate the spectrum shown in Figure 6b are $|\langle J^{(199,15N)} \rangle| = 29.0 \text{ Hz}$, $|\langle J^{(199,14N)} \rangle| = 20.6 \text{ Hz}$, and $d = 1.65 \text{ Hz}$ at 4.70 T. The agreement between
obtained and calculated spectra is good. The ratio of \(|J(199\text{Hg},13\text{C})|_\text{obs} : |J(199\text{Hg},14\text{N})|_\text{calc} = 1.41\) agrees well with the ratio of \(\gamma(13\text{C})/\gamma(14\text{N}) = 1.403\). This further confirms the results obtained from the analysis of \(199\text{Hg}\) MAS NMR spectra of an unenriched sample.

The only values of \(2J(199\text{Hg},14\text{N})\) available in the literature have been obtained for organomercury fulminates, \(\text{RHgCNO}\) \((\text{R} = \text{Me, Ph, CNO})\), in DMSO and THF solutions. It is noted that the value of \(2J(199\text{Hg},14\text{N})\) for \(\text{K}_2\text{Hg(CN)}_4\) is significantly smaller than the values reported for the mercury fulminates, 89 Hz to 65 Hz.\(^{65}\)

**15N MAS NMR Spectra.** Nitrogen-15 MAS NMR spectra of \(\text{K}_2\text{Hg(CN)}_4\) were also obtained using the partially \(^{15}\text{N}\) enriched sample (\(\approx 70\%\)). The isotropic peak, centered at 280.9 ppm, was flanked by several spinning sidebands when the magic-angle spinning frequency was in the range 2.0–4.0 kHz. Using the Herzfeld–Berger method, the principal components of the nitrogen chemical shift tensor can be recovered from the relative intensities of the spinning sidebands. Assuming that the nitrogen chemical shift tensor is axially symmetric, analysis yields \(\delta_2 = 440\) ppm and \(\delta_1 = -37\) ppm. The chemical shift anisotropy, 477 ppm, is about 70 ppm larger than typical values reported for organic nitriles.\(^{56}\) The isotropic \(^{15}\text{N}\) chemical shift of the cyano group in \(\text{K}_2\text{Hg(CN)}_4\) is approximately 30 ppm to high frequency (deshielding) of the values in organic nitriles. Comparing the principal components of the \(^{15}\text{N}\) chemical shift tensor of \(\text{K}_2\text{Hg(CN)}_4\) with those of the organic nitriles reveals that high-frequency shift is mainly due to changes in the \(\delta_2\) components. The principal components of the nitrogen chemical shift tensor in \(\text{K}_2\text{Hg(CN)}_4\) were found to be comparable to those in \(\text{NaC}_3\text{N}\), the anisotropy being approximately 460 ppm in the latter salt.\(^{59}\)

Nitrogen-15 MAS NMR spectra of \(\text{K}_2\text{Hg(CN)}_4\) at higher spinning frequencies were also recorded. The natural half-height line width of the \(^{15}\text{N}\) isotropic peak and the MAS sidebands (ca. 40 Hz) precluded resolution of \(199\text{Hg}\) satellites; however the base of each peak was broadened due to \(199\text{Hg}\) \(^{15}\text{N}\) indirect spin–spin coupling.

**Conclusions.**

Nuclear spin–spin coupling data and chemical shift parameters obtained for solid \(\text{K}_2\text{Hg(CN)}_4\) are summarized in Tables I and II, respectively. The results indicate that the indirect spin–spin interactions involving mercury are anisotropic. The magnitude of \(\Delta J(199\text{Hg},13\text{C})\) in solid \(\text{K}_2\text{Hg(CN)}_4\) is comparable to the value reported for dimethylmercury. Although values of \(\Delta J\) from the

**References and Notes.**


**TABLE I: Calculated Direct Dipolar (R_D), Observed Effective Direct Dipolar (R_{E, D}), and Indirect Spin–Spin (J) Interactions in Solid \(\text{K}_2\text{Hg(CN)}_4\)**

| spin pair | X, Y | R(X,Y)_{DD} | R(X,Y)_{eff} | |J(X,Y)|_{calc} | \Delta J(X,Y) = J_1 - J_2 |
|----------|-----|-------------|-------------|----------|----------------|----------------|
| \(^{13}\text{C}, 14\text{N}\) | 1359 | 1290±50 |           |          |               |                |
| \(^{199}\text{Hg}, 13\text{C}\) | 542  | 225±10  |          |          |               |                |
| \(^{199}\text{Hg}, 14\text{N}\) | 43.0 | 204±5   |          |          |               |                |
| \(^{199}\text{Hg}, 15\text{N}\) | -60.3 | -28±5   |          |          |               |                |

* All parameters are in Hz.

**TABLE II: Chemical Shift Parameters\(^{a,b}\) Obtained for Solid \(\text{K}_2\text{Hg(CN)}_4\)**

<table>
<thead>
<tr>
<th>nucleus</th>
<th>(\delta_{iso})</th>
<th>(\delta_1)</th>
<th>(\delta_2)</th>
<th>(\Delta \delta = \delta_2 - \delta_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{13}\text{C})</td>
<td>153.1</td>
<td>262.8</td>
<td>-66.3</td>
<td>329.1</td>
</tr>
<tr>
<td>(^{15}\text{N})</td>
<td>280.9</td>
<td>440</td>
<td>-37</td>
<td>477</td>
</tr>
<tr>
<td>(^{199}\text{Hg})</td>
<td>-463</td>
<td>-463</td>
<td>-463</td>
<td>0</td>
</tr>
</tbody>
</table>

* All values are in ppm. \(\delta_1\) and \(\delta_2\) are the chemical shifts when the applied magnetic field is parallel and perpendicular, respectively, to the \(C_3\) axis along the \(\text{Hg–C=CN}\) direction. \(^a\) Required by the site symmetry.
Anisotropic Nuclear Spin Interactions in K$_2$Hg(CN)$_4$

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