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Multinuclear NMR Study of Dipotassium Tetracyanometalates of the Group 12 Metals in the Solid State

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The carbon NMR chemical shift tensors have been measured for solid samples of $K_2[M(CN)_4]$ (M = Zn, Cd, Hg) in which the cyano ligand is partially ^{13}C enriched. The symmetry at the carbon atom in each of these salts requires that the carbon chemical shift tensor be axially symmetric. The unique component of the tensors, which is along the M−C ≡ N bond, was found to be the most shielded. The spans of the carbon chemical shift tensors were found to be very similar for the three complexes. On descending the group 12 metal cyanides, $K_2[M(CN)_4]$, from Zn to Hg, small increases in both the $\delta_\perp(^{13}C)$ and $\delta_\parallel(^{13}C)$ components were observed. Magic-angle-spinning (MAS) ^{67}Zn, ^{113}Cd, and ^{199}Hg NMR spectra were obtained for $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, and $K_2[Hg(CN)_4]$, respectively. The following values for ^1J(M,C) were found: $^1J(^{67}Zn,^{13}C)_{iso} = 88$ Hz, $^1J(^{113}Cd,^{13}C)_{iso} = 575$ Hz, and $^1J(^{199}Hg,^{13}C)_{iso} = 1540$ Hz. The measurement of $^1J(^{67}Zn,^{13}C)_{iso}$ for solid $K_2[Zn(CN)_4]$ represents the first report of an indirect spin−spin (*J*) coupling constant involving ^{67}Zn.

Introduction

Early solution-state ^{13}C NMR studies of transition-metal cyanides[1−6] have revealed different trends for the carbon chemical shifts of these complexes depending on whether or not the metals have a completely filled outer d shell. For example, in the square-planar d^8 series of metal cyanides $[M(CN)_4]^{2-}$ where M = Ni(II), Pd(II), and Pt(II), the ^{13}C nucleus of the cyano ligand becomes more shielded on descending the group 10 metals. In contrast, for the tetrahedral d^{10} series of $[M(CN)_4]^{2-}$ where M = Zn(II), Cd(II), and Hg(II), the ^{13}C nucleus of the cyano ligand becomes less shielded when M changes from Zn(II) to Cd(II) and to Hg(II). These observations have been rationalized qualitatively in terms of changes in σ and π bonding of the cyano ligand to the various metal ions.[6]

However, the aforementioned trend was established only for *isotropic* carbon chemical shifts. Given the anisotropic nature of the chemical shielding interaction, it should be more instructive to investigate the chemical shift *tensors* instead of their traces, *i.e.*, average values. The lack of data on carbon chemical shift tensors for metal−cyano complexes may seem rather surprising. However, it should be noted that it is difficult to obtain high-quality ^{13}C NMR spectra because the ^{13}C relaxation times are long in solids and cross-polarization from protons is not possible since a proton reservoir is unavailable. In addition, the spectra are complicated by dipolar interactions with neighbouring ^{14}N nuclei. To date, there have been only a few scattered studies in the literature reporting carbon chemical shift tensors for metal−cyanide complexes.[7−11] Among these studies, only the recent report by Kim and Butler[10] details systematic variations in the carbon chemical shift tensors of the three group 10 square-planar d^8 metal−cyano complexes $[M(CN)_4]^{2-}$ where M = Ni(II), Pd(II), and Pt(II). They found that, on descending the group, changes in the carbon chemical shift tensor component perpendicular to the M−C≡N bond are primarily responsible for decreases in the *isotropic* chemical shift observed in earlier solution-state NMR studies.

Here we report the results of a multinuclear solid-state NMR study of the complete series of $K_2[M(CN)_4]$ salts where M = Zn(II), Cd(II), and Hg(II). It is important to characterize the carbon chemical shift tensors for these complexes since they are typical complexes with filled d shells. Moreover, previous X-ray and neutron diffraction studies indicate that these group 12 tetrahedral metal cyanide salts are cubic at room temperature,[12−15] providing the necessary site symmetry to investigate NMR parameters involving both the cyano ligand and the metal nucleus. Our recent study of solid $K_2[Hg(CN)_4]$ demonstrates the feasibility of such an analysis.[11,16]

Experimental Section

Partially ^{13}C enriched samples of $K_2[M(CN)_4]$ (M = Zn, Cd) were prepared by dissolving a 1:2 molar ratio of $M(CN)_2$ (M = Zn, Cd) and KCN (a mixture of KCN and $K^{13}CN$) in aqueous solution and then evaporating the water. The partially ^{13}C enriched sample of $K_2[Hg(CN)_4]$ was prepared by dissolving 0.020 mol of KCN (a mixture of KCN and $K^{13}CN$) and 0.010 mol of $Hg(CN)_2$ in methanol and then evaporating the solvent. The ^{13}C enrichment was approximately 25%, 14%, and 40% for $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, and $K_2[Hg(CN)_4]$, respectively.

All solid-state NMR experiments were carried out on Bruker MSL-200 (4.70 T) and AMX-400 (9.40 T) NMR spectrometers.

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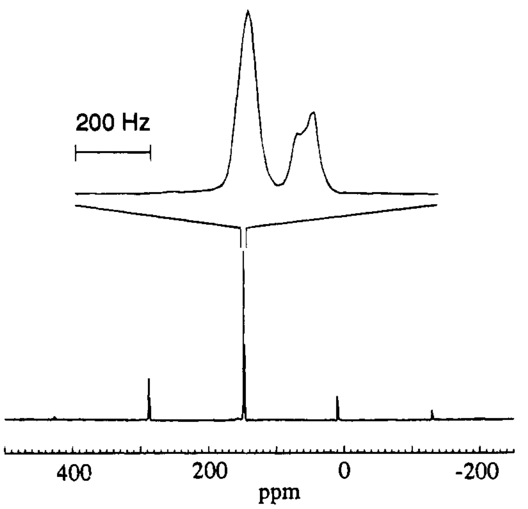

Figure 1. ^{13}C MAS NMR spectrum of a powder sample of $K_2[Zn(CN)_4]$ obtained at 9.40 T. Sample spinning frequency: 13 989 Hz. Recycle time: 60 s. Number of scans: 64.

In the ^{13}C MAS NMR experiments, the recycle time was 60 s. The spin-echo sequence[17] was used for obtaining static ^{13}C NMR spectra, and the recycle time was 20 min due to the long ^{13}C spin−lattice relaxation time. Carbon-13 chemical shifts were referenced with respect to TMS using solid adamantane as a secondary reference.[18]

Zinc-67 MAS NMR spectra were obtained at 25.04 MHz using the 9.40 T magnet. Zinc-67 chemical shifts were referenced to 1.0 M $Zn(NO_3)_2$ aqueous solution.[19] The ^{67}Zn spin−lattice relaxation time in solid $K_2[Zn(CN)_4]$ was determined using the conventional inversion-recovery method.

Cadmium-113 MAS NMR spectra were obtained at 44.42 MHz using the MSL-200. Cadmium-113 chemical shifts were referenced to 0.1 M $Cd(ClO_4)_2$ aqueous solution by setting the ^{113}Cd NMR signal of solid $Cd(NO_3)_2 \cdot 4H_2O$ to −100 ppm.[20]

Mercury-199 MAS NMR spectra were obtained at 4.70 T operating at 35.83 MHz for ^{199}Hg nuclei. Mercury-199 chemical shifts were referenced to $Hg(CH_3)_2$ by comparing the observed ^{199}Hg NMR frequency of solid $K_2[Hg(CN)_4]$ with that of $Hg(CH_3)_2$, which is 17.910 841 MHz in a magnetic field in which the protons of TMS resonate at exactly 100 MHz.[21]

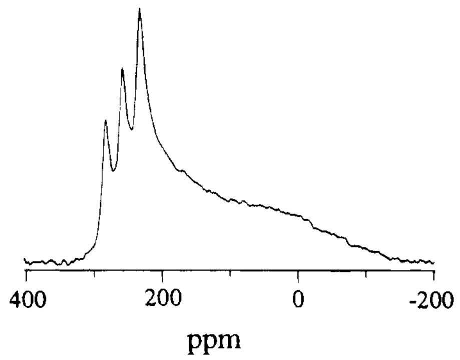

Figure 2. Static ^{13}C NMR spectrum of a powder sample of $K_2[Zn(CN)_4]$ obtained at 4.70 T. Recycle time: 20 min. Number of scans: 575.

Table 1. Chemical Shift Parameters Obtained for Solid $K_2[M(CN)_4]$ (M = Zn, Cd, Hg)[a,b]

	^{13}C				metal	
	δ_{iso}	$\delta_{\perp}$[c]	$\delta_{\parallel}$[c]	Ω[d]	δ_{iso}[e]	σ_{iso}[f]
^{67}Zn	148.7 (147.0)	259	−72	331	291 (283)	−981
^{113}Cd	149.7 (149.8)	259	−69	328	569 (510)	−1674
^{199}Hg	153.1 (153.2)	263	−66	329	−463 (−480)	−4220

[a] All values are in ppm. [b] Chemical shifts observed in aqueous solutions are given in parentheses. [c] $\delta_{\perp}$ and $\delta_{\parallel}$ are the chemical shifts when the applied magnetic field is perpendicular and parallel to the C_3 axis along the M−C≡N direction, respectively. [d] Span $\Omega = \delta_{\perp} - \delta_{\parallel}$. [e] ^{67}Zn, ^{113}Cd, and ^{199}Hg chemical shifts relative to 1.0 M $Zn(NO_3)_2$ in H_2O, 0.1 M $Cd(ClO_4)_2$ in H_2O, and neat $Hg(CH_3)_2$, respectively. [f] Chemical shieldings relative to free atoms converted using the data quoted in ref 31.

Results and Discussion

The ^{13}C MAS NMR spectrum of $K_2[Zn(CN)_4]$ is shown in Figure 1. The observed asymmetric doublet is typical for ^{13}C nuclei directly bonded to ^{14}N ($I = 1$).[22] From the observed ^{13}C MAS NMR spectrum, the isotropic carbon chemical shift can be accurately determined. However, it is more difficult to extract the principal components of the carbon chemical shift tensor from the spinning sideband intensities since the ^{13}C MAS NMR spectra are modulated by both the anisotropic chemical shift and $^{13}C-^{14}N$ dipolar interactions. Therefore, static ^{13}C NMR powder patterns were acquired for this purpose. In Figure 2, the static ^{13}C NMR spectrum for $K_2[Zn(CN)_4]$ is shown. Since the ^{13}C spin−lattice relaxation time is very long and highly anisotropic (*i.e.*, the low-frequency end of the ^{13}C NMR powder pattern has a longer relaxation time than the high-frequency end), a long recycle time of 20 min was used. In the static ^{13}C NMR spectrum, three subspectra arising from the three spin states of the directly bonded ^{14}N nucleus are clearly observed. From the central subspectrum of Figure 2, $\delta_{\perp} = 259 \pm 2$ ppm and $\delta_{\parallel} = -72 \pm 2$ ppm were directly obtained for $K_2[Zn(CN)_4]$. The splittings between each of the three adjacent low-frequency shoulders of the static spectrum equal twice the $^{13}C-^{14}N$ dipolar coupling constant.[23] From the experimental spectrum shown in Figure 2, a value of 1.37 ± 0.10 kHz was determined for the $^{13}C-^{14}N$ dipolar coupling constant in solid $K_2[Zn(CN)_4]$. This value is in good agreement with the calculated value, 1.41 kHz, based upon the C−N distance of 1.157 Å.[15] For $K_2[Cd(CN)_4]$ and $K_2[Hg(CN)_4]$, only the perpendicular components, $\delta_{\perp}$, were directly determined from the static ^{13}C NMR spectra because of the low signal-to-noise ratio. The parallel components, $\delta_{\parallel}$, for these two complexes were then calculated using the observed $\delta_{\perp}$ components and the values of δ_{iso} which can be accurately determined from the ^{13}C MAS NMR spectra. The carbon chemical shift parameters for the three complexes are given in Table 1. The isotropic carbon chemical shifts found for all three solid metal−cyanide complexes are in good agreement with the values obtained in the solution-state NMR study.[6] All isotropic carbon chemical shifts for the metal complexes were found to be more shielded (at lower frequencies) than that found for the "free" CN^- ligand, 166.2 ppm.[6] From the data given in Table 1, it is also apparent that the isotropic carbon chemical shifts increase slightly as the metal atom is varied from zinc to cadmium to mercury, as observed previously in solution NMR studies. Interestingly, from the data shown in Table 1, small increases in the carbon chemical shifts are observed in both the $\delta_{\perp}$ and $\delta_{\parallel}$ components as one descends the group 12 metals. This indicates that the observed increase in the isotropic carbon chemical shift on descending the group 12 metals is caused by

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Table 2. Indirect Spin–Spin Coupling Parameters[a] for Solid $K_2[M(CN)_4]$ (M = Zn, Cd, Hg)

	$K_2[M(CN)_4]$			$M(CH_3)_2$[b]		
M	$^1J(M,^{13}C)_{iso}$	$^1K(M,^{13}C)_{iso}$	$K_\parallel - K_\perp$	$^1J(M,^{13}C)_{iso}$	$^1K(M,^{13}C)_{iso}$	$K_\parallel - K_\perp$
^{67}Zn	88	465				
^{113}Cd	(−)575	855		−536	797	279
^{199}Hg	1540	2832	1747[c]	687	1263	599

[a] All coupling constants are in Hz and all reduced coupling constants are in the SI units of $10^{19} \times N A^{-2} m^{-3}$. [b] From refs 37 and 38. [c] From ref 11.

increases in both the perpendicular and parallel components of the carbon chemical shift tensor. This is clearly in contrast to the situation in the square-planar complexes $[M(CN)_4]^{2-}$ with unfilled valence d shells.[10] Also, for the square-planar d^8 complexes, it was found that the $\delta_\perp$ components of the carbon chemical shift tensor are more sensitive to the nature of the group 10 metal.

The T_d symmetry at the metal center in solid $K_2[M(CN)_4]$ complexes also makes it feasible to obtain NMR spectra arising from the metal nucleus, since the chemical shift anisotropy vanishes. As well, the electric field gradient at the quadrupolar ^{67}Zn nucleus ($I = {}^5/_2$) is zero. The chemical shift parameters for the metal nuclei are also given in Table 1. It is interesting to note that in Table 1 the metal chemical shift measured in the solid sample is always greater than the value obtained in aqueous solution, indicating that the metal ion experiences a less shielded environment in the crystal lattice. This is quite a general observation,[24,25] the origin of which remains unclear.

Since there have been recent interests in calculating chemical shieldings for group 12 metals,[26–30] it is more useful to report the observed chemical shifts on a common scale, i.e., relative to their respective free atoms. In Table 1, the observed chemical shifts for metal nuclei have been converted to the chemical shieldings. Although the reliability of current theoretical calculations of chemical shielding involving heavy elements may seem unclear, the experimental chemical shielding values reported here will be useful for testing the quality of future *ab initio* MO calculations.

The ^{67}Zn, ^{113}Cd, and ^{199}Hg MAS NMR spectra for solid $K_2[Zn(CN)_4]$, $K_2[Cd(CN)_4]$, and $K_2[Hg(CN)_4]$, respectively, are shown in Figure 3. Zinc-67 is not an easy nucleus to detect by NMR because of its low magnetogyric ratio, low natural abundance, 4.11%, and relatively large quadrupole moment, 0.16×10^{-28} m^2. Accordingly, the number of solution-state ^{67}Zn NMR studies is rather small, most of these dealing only with highly symmetric species.[19,32–34] Only two solid-state ^{67}Zn NMR studies have appeared in the literature,[35,36] and to the best of our knowledge no *J*-coupling involving ^{67}Zn nuclei has ever been reported. In Figure 3a, the observed multiplet in the ^{67}Zn MAS NMR spectrum can be simulated with $^1J(^{67}Zn,^{13}C) = 88$ Hz (note that, since the level of ^{13}C enrichment is 25%, one must also consider the presence of anions with more than one ^{13}C-labeled cyano group). It was not possible to measure $^1J(^{67}Zn,^{13}C)$ from the ^{13}C MAS NMR spectrum of $K_2[Zn(CN)_4]$, due, in part, to the residual $^{13}C-^{14}N$ dipolar coupling. This difficulty is enhanced by the low natural abundance of ^{67}Zn and the anticipated splitting arising from a spin ${}^5/_2$ nucleus. Measurement of the ^{67}Zn spin–lattice relaxation time for solid $K_2[Zn(CN)_4]$ indicates that $T_1(^{67}Zn) = 0.77$ s; thus self-decoupling is not responsible for the failure to detect $^1J(^{67}Zn,^{13}C)$ in the ^{13}C MAS NMR spectrum of $K_2[Zn(CN)_4]$.

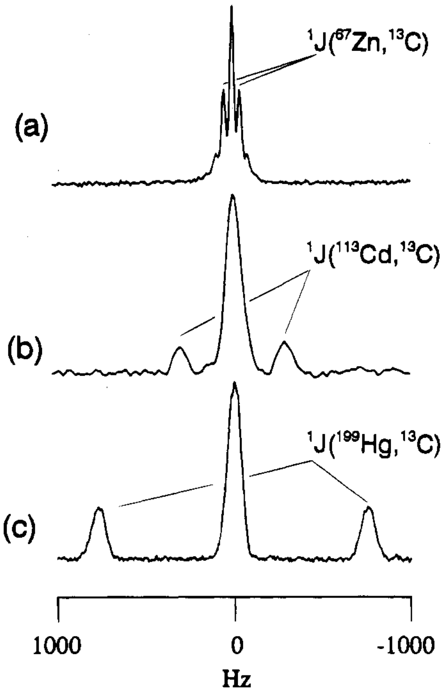

Figure 3. MAS NMR spectra of the metal nuclei for solid $K_2[M(CN)_4]$. (a) ^{67}Zn MAS NMR spectrum obtained at 9.40 T. Recycle time: 2 s. Number of scans: 2048. Sample spinning frequency: 4050 Hz. (b) ^{113}Cd MAS NMR spectrum obtained at 4.70 T. Recycle time: 60 s. Number of scans: 51. Sample spinning frequency: 3000 Hz. (c) ^{199}Hg MAS NMR spectrum obtained at 4.70 T. Recycle time: 30 s. Number of scans: 936. Sample spinning frequency: 2731 Hz.

The line width of the peaks in the ^{67}Zn MAS NMR spectrum shown in Figure 3a is 23 Hz. It is interesting to note that this line width is approximately half of that observed for an aqueous solution of $K_2[Zn(CN)_4]$.[19] Similar observations were reported in our previous ^{201}Hg ($I = {}^3/_2$) NMR study[16] of $K_2[Hg(CN)_4]$. Although a ^{201}Hg NMR signal can be readily detected for solid $K_2[Hg(CN)_4]$, it is too broad to be detected in aqueous solution. The line width of the peaks in the ^{67}Zn MAS NMR spectrum for $K_2[Zn(CN)_4]$ is also much smaller than the corresponding values in the ^{113}Cd and ^{199}Hg MAS NMR spectra for $K_2[Cd(CN)_4]$ and $K_2[Hg(CN)_4]$, respectively. It has been shown in a previous study[11] that, in the case of $[Hg(CN)_4]^{2-}$, the line broadening in the ^{199}Hg MAS NMR spectrum is primarily due to the *J* and residual dipolar couplings to the four neighboring

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^{14}N nuclei. For $K_2[Hg(CN)_4]$, $^2J(^{199}Hg,^{14}N)_{iso} = 20.6$ Hz was observed.[11] Since ^{67}Zn has a much lower magnetogyric ratio, γ, than ^{199}Hg, both the J and dipolar coupling to the ^{14}N nuclei are expected to be much smaller for $[Zn(CN)_4]^{2-}$. From Figure 3b,c $^1J(^{113}Cd,^{13}C)_{iso}$ and $^1J(^{199}Hg,^{13}C)_{iso}$ can also be determined directly. It is most convenient to compare J-coupling constants expressed as reduced coupling constants, $K(X,Y)$, which are defined by eq 1, where h is Planck's constant. The observed

$$K(X,Y) = \frac{J(X,Y)}{h}\left(\frac{2\pi}{\gamma_X}\right)\left(\frac{2\pi}{\gamma_Y}\right) \qquad (1)$$

J-coupling parameters for the three metal–cyano complexes are given in Table 2. For comparison, data for $Cd(CH_3)_2$ and $Hg(CH_3)_2$ taken from the literature[37,38] are also included in Table 2. Since $^1K(Hg,C)_{iso}$ and $^1K(Cd,C)_{iso}$ are known to be positive,[39] the sign of $^1K(Zn,C)_{iso}$ and hence $^1J(^{67}Zn,^{13}C)_{iso}$ is expected to be positive. In Table 2, it is found that the values of $^1K(M,C)_{iso}$ increase with the atomic number of the metal; this is a general observation.[40–43] It is interesting to note that, while the magnitude of $^1K(Cd,C)_{iso}$ is similar for $K_2[Cd(CN)_4]$ and $Cd(CH_3)_2$, $^1K(Hg,C)_{iso}$ for $K_2Hg(CN)_4$ is greater than that for $Hg(CH_3)_2$ by more than a factor of 2. In a previous study, we have shown that $^1J(^{199}Hg,^{13}C)$ is anisotropic.[11] However, the static ^{67}Zn and ^{113}Cd NMR spectra for $K_2[Zn(CN)_4]$ and $K_2[Cd(CN)_4]$, respectively, are difficult to analyze because of spectral overlaps. Hence, no conclusion about the anisotropy in $^1J(^{67}Zn,^{13}C)$ and $^1J(^{113}Cd,^{13}C)$ can be reached at this time. Single-crystal NMR studies will be useful in solving this problem. It is known from a previous theoretical study[37] that the relativistic effects result in a larger relative anisotropy, $(K_{\parallel} - K_{\perp})/K_{iso}$, for $^1K(Hg,C)$ than for $^1K(Cd,C)$. The relative J-anisotropy found in $K_2[Hg(CN)_4]$, 0.62, is comparable to the value of 0.47 that was determined for $Hg(CH_3)_2$. Unfortunately, considering the difficulties that are involved in calculating indirect spin–spin coupling tensors, especially with heavy elements, reliable calculations still remain a formidable, if not an impossible, task. Nevertheless, the observed values for $^1J(M,^{13}C)$ in this series of metal–cyano complexes will serve as a test for any theoretical attempt as well as a challenge to theoreticians.

Conclusions

The carbon chemical shift tensors have been measured for $K_2[M(CN)_4]$ (M = Zn, Cd, Hg) in the solid state. In these complexes with completely filled d shells, the small increase in the isotropic carbon chemical shift as one descends the group 12 metals results from an increase in the chemical shift components both perpendicular and parallel to the $M-C\equiv N$ bond. The first J-coupling constant involving ^{67}Zn nuclei is reported for solid $K_2[Zn(CN)_4]$. The values of $^1K(M,^{13}C)_{iso}$ found in the series $K_2[M(CN)_4]$ (M = Zn, Cd, Hg) increase with the atomic number of the metal.

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