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Solid-State ^{13}C NMR Chemical Shift Tensors in Square-Planar Tetracyanometalates (M = Ni, Pd, Pt)

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The principal elements of the ^{13}C NMR chemical shift tensors have been determined for three square-planar tetracyanometalates, $K_2Ni(CN)_4\cdot H_2O$, $K_2Pd(CN)_4\cdot 3H_2O$, and $K_2Pt(CN)_4\cdot 3H_2O$, from the solid-state ^{13}C NMR powder patterns. The orientation of the ^{13}C chemical shift tensor is partially assigned on the basis of the dipolar coupling analysis to ^{14}N. The chemical shift tensors are nearly axial and for all three complexes have almost the same values and, in turn, are quite similar to the values for acetonitrile. The most shielded element, about −90 ppm, is aligned with the M–CN vector.

Introduction

There has been much discussion of the relationship between ^{13}C NMR chemical shifts and metal–ligand bonding.[1–6] Some of the factors considered are charge transfer to the ligand and metal–ligand multiple bonding. Unfortunately, much of the data are based on solution-state NMR measurements; hence, only the isotropic chemical shift is available for interpretation. In contrast, solid-state NMR yields the principal elements of the chemical shift tensor,[7–15] thus increasing the information content of the experiment. A pioneering example of this approach is the work of Mahnke, Sheline, and Spiess and their analysis of the ^{13}C chemical shift tensors in $Ni(CO)_4$ and $Fe(CO)_5$.[3] These experiments include both solid-state ^{13}C NMR and solution-state ^{13}C T_1 measurements; the latter is done to measure the spin-rotation relaxation rate and, from this, to extract the paramagnetic contribution to the chemical shift tensor. The paramagnetic term is useful in that it is generally more dependent upon bonding than the other term, the diamagnetic contribution to the chemical shift tensor. For example, the ^{13}C chemical shift tensor for the bridging methylene unit in $(\mu\text{-}CH_2)(\mu\text{-}CO)[FeCp(CO)]_2$ is discussed in terms of large, anisotropic elements in the paramagnetic term of the chemical shift tensor.[16]

The isotropic chemical shifts of 19 diamagnetic cyano–metal complexes, ranging from linear dicyano to octahedral hexacyano complexes, were measured by Pesek and Mason.[17] Shifts range from 177.2 ppm for $Fe(CN)_6^{4-}$ to 84.7 ppm for $Pt(CN)_6^{4-}$; uncoordinated CN^- resonates at 166.2 ppm in D_2O. We find it curious that for the square-planar tetracyanometalates, the isotropic chemical shift varies only slightly: Ni, 136.6 ppm; Pd, 131.9 ppm; Pt, 125.7 ppm. We thought that an inspection of the chemical shift tensor might reveal more substantial variations in one or more principal elements, variations that might be more strongly correlated with changes in metal–ligand bonding. For this reason, we acquired the solid-state ^{13}C NMR spectra of three tetracyanometalates (M = Ni, Pd, Pt). We find, as one might expect, that the chemical shift tensor is nearly axial and the most shielded element is aligned with the M–CN vector. Surprisingly, there are only small differences in the shift elements on going from Ni to Pt, and all chemical shift tensors are rather similar to that of acetonitrile.[18]

Experimental Methods

Sample Preparation. $K_2Ni(CN)_4\cdot H_2O$ was made by the literature method[19] from $NiSO_4\cdot 6H_2O$ (Aldrich) and KCN (99% ^{13}C enrichment, Isotec). $K_2Pd(CN)_4\cdot 3H_2O$ and $K_2Pt(CN)_4\cdot 3H_2O$ were made by analogous procedures from $PdSO_4$ (Aldrich) and $K_2Pt(NO_2)_4$ (Aldrich).

Solid-State ^{13}C NMR Spectroscopy. Solid-state ^{13}C NMR powder patterns were taken on stationary samples with a Bruker MSL200 solid-state NMR spectrometer operating at 50.3 MHz for ^{13}C and using a high-power solenoidal probe. The 90° pulse length was 2 μs, and the spectra were acquired as simple Bloch decays. The ^{13}C chemical shift values recorded on the δ-scale are referenced through benzene (128.7 ppm, external) to TMS.

Exponentially filtered (200 Hz), Fourier-transformed, and manually phased spectra were transferred as binary files from the Bruker Aspect-3000 computer to a Macintosh II computer via an RS-232 serial connection and the KERMIT file transfer program. Conversion from binary to ASCII data files was done with a program[20] written in LabVIEW, a graphical programming language.[21] Spectral simulation programs[22] were written in Matlab, vector-oriented programming language.[23] The Levenberg–Marquardt nonlinear least-squares algorithm[24,25] was recoded

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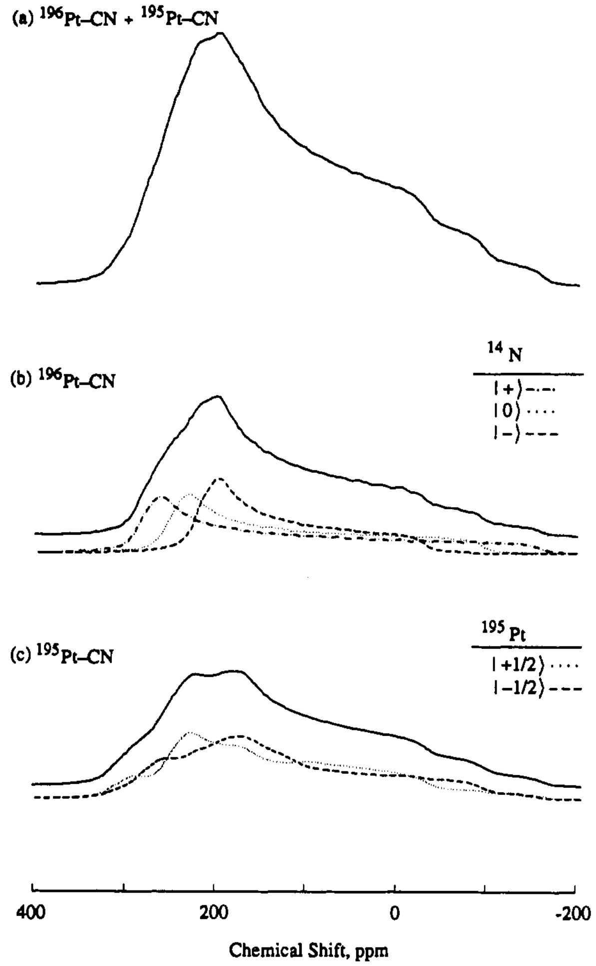

Figure 1. Calculated ^{13}C powder pattern for $K_2Pt(CN)_4{\cdot}3H_2O$. Important parameters in this calculation are as follows: $\delta_{11} = 251.8$, $\delta_{22} = 226.2$, $\delta_{33} = -94.2$ ppm; d(C–N) = 1.159, d(Pt–C) = 1.989 Å; $e^2q_{zz}Q/h$ (^{14}N) = 3.467 MHz; $\eta = 0.032$. (a) The ^{13}C powder pattern is composed of two components; the relative intensities from two isotopomers, ^{196}Pt–^{13}C^{14}N and ^{195}Pt–^{13}C^{14}N, are 66.2:33.8. (Here, we use ^{196}Pt to represent all the $S = 0$ isotopomers of Pt.) (b) The spectrum calculated for the ^{196}Pt–^{13}C^{14}N isotopomer is shown. The ^{13}C–^{14}N dipolar coupling splits the ^{13}C resonance into three subspectra. (c) The spectrum calculated for the ^{195}Pt–^{13}C^{14}N isotopomer is shown. The ^{195}Pt–^{13}C dipolar coupling splits the ^{13}C resonance into two subspectra.

in Matlab. In addition to scaling parameters, the variables in the fits are δ_{11} and δ_{33}; the value of δ_{22} is determined from δ_{11} and δ_{33} and the isotropic chemical shift.

Isotropic ^{13}C chemical shifts were acquired for the tetracyanometalates with ^{13}C MAS NMR and referenced through adamantane (28.3 ppm, external) to TMS. The ^{13}C MAS line shape of each sideband is affected by dipolar coupling to ^{14}N, but the isotropic chemical shift remains basically unchanged.[26,27]

Spectroscopy of the $M(CN)_4{}^{2-}$ (M = Ni, Pd, Pt) System. The major components of the time-independent Hamiltonian for the M–CN system include the ^{13}C Zeeman and chemical shift interactions, ^{14}N Zeeman and quadrupolar interactions, and ^{13}C–^{14}N dipolar coupling. If the metal has an isotope of appreciable abundance with $S > 0$ and a relatively large gyromagnetic ratio, then M–^{13}C dipolar and, possibly, J coupling must be included.

In the case of $[Pt(CN)_4]^{2-}$, the total Hamiltonian for the interactions experienced by the ^{13}C nucleus is

$$H_{\text{total}} = H_{\text{CS}}^{\text{C}} + H_{\text{Z}}^{\text{N}} + H_{\text{Q}}^{\text{N}} + H_{\text{D}}^{\text{CN}} + H_{\text{Z}}^{\text{Pt}} + H_{\text{D}}^{\text{PtC}} + H_{J}^{\text{PtC}} \qquad (1)$$

where the ^{13}C Zeeman and chemical shift interaction with the static

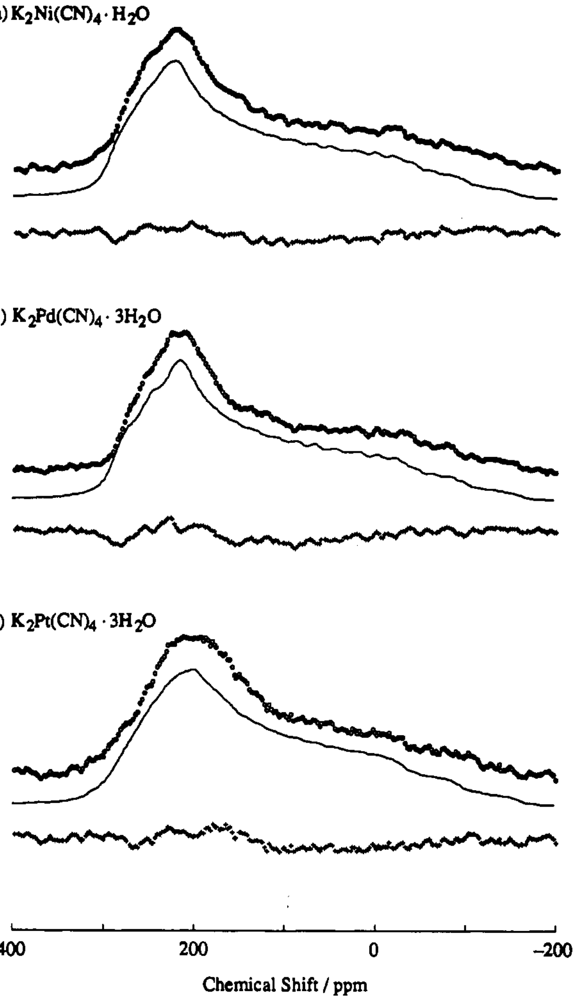

Figure 2. Solid-state ^{13}C chemical shift powder patterns and the corresponding nonlinear least-squares fits. Circles (○), solid lines (—), and crosses (+) represent the experimental ^{13}C chemical shift powder pattern, the best calculated fit, and the residual between the experimental spectrum and the fit, respectively. Experimental parameters are as follows (NS = number of scans, RD = recycle time): (a) $K_2Ni(CN)_4{\cdot}H_2O$, NS = 528, RD = 120 s, $\chi_\nu{}^2 = 1.8$; (b) $K_2Pd(CN)_4{\cdot}3H_2O$, 604, 120 s, 2.0; (c) $K_2Pt(CN)_4{\cdot}3H_2O$, 520, 120 s, 1.3.

magnetic field along the laboratory z-axis, B_z^0, is expressed by

$$H_{\text{CS}}^{\text{C}} = -\hbar\gamma^{\text{C}}B_z^0(1 + \delta_{\text{Lab}}^{zz})\,\mathbf{I}_z^{\text{C}} \qquad (2)$$

The ^{13}C resonance of the CN group is affected by not only the quadrupole-perturbed Zeeman states of ^{14}N but also by the ^{13}C–^{14}N dipolar interaction in the Hamiltonian

$$H_{\text{Z}}^{\text{N}} + H_{\text{Q}}^{\text{N}} + H_{\text{D}}^{\text{CN}} = -\hbar\gamma^{\text{N}}B_z^0(1 + \delta_{\text{iso}}^{\text{N}})\,\mathbf{S}_z^{\text{N}} + \frac{eQ/\hbar}{6I(2I-1)}\sum_{kj} eq_{kj}^{\text{Lab}} \times$$
$$[{}^3/_2(\mathbf{S}_k^{\text{N}}\mathbf{S}_j^{\text{N}} + \mathbf{S}_j^{\text{N}}\mathbf{S}_k^{\text{N}}) - \delta_{kj}\mathbf{S}^{\text{N}2}] + \left\{\frac{\gamma^{\text{C}}\gamma^{\text{N}}\hbar}{|\mathbf{r}_{\text{Lab}}^{\text{CN}}|^3}[\mathbf{I}_x^{\text{C}}\mathbf{S}_x^{\text{N}} + \mathbf{I}_y^{\text{C}}\mathbf{S}_y^{\text{N}} + \mathbf{I}_z^{\text{C}}\mathbf{S}_z^{\text{N}}] - \right.$$
$$\left. 3\frac{\gamma^{\text{C}}\gamma^{\text{N}}\hbar}{|\mathbf{r}_{\text{Lab}}^{\text{CN}}|^5}\{[\mathbf{I}_x^{\text{C}}r_x + \mathbf{I}_y^{\text{C}}r_y + \mathbf{I}_z^{\text{C}}r_z][\mathbf{S}_x^{\text{N}}r_x + \mathbf{S}_y^{\text{N}}r_y + \mathbf{S}_z^{\text{N}}r_z]\}\right\} \qquad (3)$$

where the ^{15}N isotropic chemical shift, $\delta_{\text{iso}}^{\text{N}}$, is 105.5 (2) ppm relative to $NaNO_3$.[28] The ^{15}N chemical shift anisotropy[29,30] of the cyanide group in $(CH_3)_3C(C_6H_4)C{\equiv}N$[31] is 384 ppm, which has a negligible effect on the ^{13}C NMR powder pattern. The ^{14}N quadrupole coupling constant,

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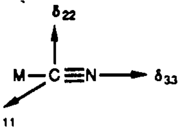
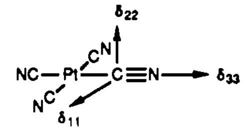
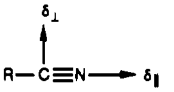
Table I. Solid-State ^{13}C NMR Chemical Shift Tensors for Tetracyanometalates

compd	solid state δ_{11}	solid state δ_{22}	solid state δ_{33}	orientation	solid state δ_{iso}	solution state[a] δ_{iso}	F_{MC}[b] (mdyn Å^{-1})	Δ_1[c] (cm^{-1})
$K_2Ni(CN)_4 \cdot H_2O$	265.9 (3)	242.9 (3)	−92.7 (3)		138.7	136.6	2.25 (2)	33 800
$K_2Pd(CN)_4 \cdot 3H_2O$	258.5 (3)	236.0 (3)	−94.9 (3)		133.2	131.9	2.32 (2)	44 600
$K_2Pt(CN)_4 \cdot 3H_2O$	251.8 (5)	226.2 (5)	−94.2 (4)		127.9	125.7	2.75 (1)	>50 000
$K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$[d]	225 (10)	187 (5)	−84 (10)		109			
HCN[e]	222	222	−112		111			
CH_3CN[f]	224	224	−96		117			

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$e^2q_{zz}Q/h$, for $K_2[Pt(CN)_4] \cdot 3H_2O$ is 3.467 MHz, and the asymmetry parameter, η, is 0.032;[32] the same values were used in the analysis of Ni and Pd complexes. The ^{14}N quadrupole interaction perturbs the ^{13}C NMR powder pattern when the ^{14}N quadrupole interaction is comparable in size to the ^{14}N Zeeman interaction; the ^{14}N Larmor frequency is 14.448 MHz at 4.7 T. The partial assignment of the ^{13}C chemical shift tensor orientation is based on the ^{13}C–^{14}N dipolar coupling. The C–N bond distance of 1.159 Å from the X-ray crystallographic studies for $K_2[Pt(CN)_4] \cdot 3H_2O$[33,34] was used in the calculation of the ^{13}C powder patterns. The C–N bond distances are 1.13 Å for $K_2[Ni(CN)_4]$[33] and 1.16 Å for $Na_2[Pd(CN)_4] \cdot 2H_2O$.[35] In the calculations for the Ni and Pd complexes, quadrupole interactions from the $S = {}^3/_2$ ^{61}Ni isotopomer (1.19%) and $S = {}^5/_2$ ^{105}Pd isotopomer (22.23%) are ignored.

The ^{195}Pt–^{13}C dipolar and ^{195}Pt Zeeman interactions are similar to those given in eq 3. The ^{195}Pt isotropic chemical shift for $K_2[Pt(CN)_4]$ is 4713 ppm relative to H_2PtCl_6.[36] Even though the ^{195}Pt chemical shift anisotropy can be quite large for square-planar complexes, 9100 ppm in $Ba[Pt(CN)_4] \cdot 2H_2O$[37] and 10 340 ppm in K_2PtCl_4,[38] ^{195}Pt chemical shift anisotropy does not significantly affect the ^{13}C NMR powder pattern. The Pt–C bond distance is 1.989 (2) Å.[34] The ^{195}Pt–^{13}C isotropic J coupling is given by

$$H_J^{PtC} = J(I_x^C S_x^{Pt} + I_y^C S_y^{Pt} + I_z^C S_z^{Pt}) \qquad (4)$$

The isotropic J coupling constant between the ^{13}C and ^{195}Pt nucleus, 1300 Hz, is measured from the ^{13}C MAS spectrum. No corrections are made for J anisotropy; if the J anisotropy is similar to that found for the ^{199}Hg–^{31}P system,[39] then the effect on the ^{13}C powder pattern is negligible.

After each Hamiltonian term has been expanded for the uncoupled product basis set of $|^{14}N\ ^{195}Pt\ ^{13}C\rangle$ by direct product expansion from Pauli spin matrices, the resulting 12 × 12 matrices are added to obtain the total Hamiltonian matrix. The eigenenergies are obtained by diagonalization. The six single-quantum ^{13}C transitions are used to generate the ^{13}C powder pattern over the two Euler angles, θ and χ, where the angles are incremented by a uniform step angle of 2° within the range of 0–90° and with sin θ weighting.[22] Figure 1 shows a calcualted ^{13}C powder pattern for $[Pt(CN)_4]^{2-}$, in which both ^{13}C–^{14}N and ^{195}Pt–^{13}C interactions are considered and the orientation of the largest principal element of the ^{14}N electric field gradient tensor, eq_{zz}, coincides with the C–N bond direction.

Results

The ^{13}C NMR powder patterns for $K_2Ni(CN)_4 \cdot H_2O$, $K_2Pd(CN)_4 \cdot 3H_2O$, and $K_2Pt(CN)_4 \cdot 3H_2O$ are shown in Figure 2. Also shown are the nonlinear least-squares fits of a simulated spectrum to each experimental spectrum. On the basis of the ^{13}C–^{14}N dipolar coupling, δ_{33} is required to be aligned with the M–CN vector. In a single-crystal NMR study of $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$,[40] the orientation of the ^{13}C chemical shift tensor relative to the molecular axis was assigned. On the basis of the similar values for δ_{11} and δ_{22} found here, the same orientation is likely with δ_{22} perpendicular to the plane of the square-planar metal complex and δ_{11} perpendicular to the CN bond axis and in the plane of the metal complex. The assignment of the orientations of δ_{11} and δ_{22} is tentative; single-crysal NMR studies could be used to confirm the assignment. Table I shows the solid-state ^{13}C chemical shift tensor elements and their orientations relative to the molecular framework.

Discussion

The ^{13}C chemical shift tensors show the following trends. The isotropic ^{13}C chemical shift is essentially the same in solution as in the solid state. There is a small upfield shift (more negative values on the δ scale) in δ_{11} and δ_{22} on going from Ni to Pt, and that effect has been noted earlier for δ_{iso}.[17] The value of δ_{33} is nearly constant, changing by less than 3 ppm for the series. In all three metal complexes, the chemical shift tensor is nearly axial and has values rather similar to other nitriles, hydrogen cyanide, and acetonitrile, as listed in Table I. The similarity between metal-bound cyanide and the organic nitriles is analogous to the situation for CO as a ligand. Often, there is only a small difference between the ^{13}C chemical shift tensors for free and metal-bound carbonyl.[7,29,30,41]

Also listed in Table I are two other parameters used here as qualitative markers for trends in the M–CN bonding. The metal–carbon vibrational stretching force constant, F_{MC}, was determined from a force field analysis by Kubas and Jones[42] and shows somewhat stronger metal–carbon bonding in the tetracyanoplatinate complex than for Ni or Pd. A ligand field parameter,

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Δ_1, is derived from d–d transitions in the electronic absorption spectrum and is the difference between the $b_{1g}(x^2-y^2)$ and $b_{2g}(xy)$ orbital energies in a square-planar metal complex. Δ_1 is used here as a measure of σ and π bond interactions between the metal and the ligand.[43,44] There does not seem to be any substantial correlation between the values of δ_1 and δ_{22} and these measures of metal–carbon bonding, though such correlations may be masked in transition metal complexes by competing factors.[4]

The separation of the chemical shift tensor into two components, the diamagnetic and paramagnetic contributions, may aid in the understanding of the trends, or lack of, for the chemical shifts in different metal complexes. Unfortunately, the extraction of the paramagnetic contribution, which is most convincingly done with the measurement of the spin-rotation relaxation rate,[3] does not appear to be possible, on the basis of a preliminary analysis by Pesek and Mason.[17] A second route for separating the chemical shift tensor is the calculation of the diamagnetic contribution, either by estimation[45–47] or by ab initio molecular orbital methods.[48–51]

Conclusions

The principal elements and the relative orientations of the ^{13}C chemical shift tensor have been obtained for tetracyanometalates (M = Ni, Pd, Pt) in the solid state. The chemical shift tensor is nearly axial, and, on the basis of the dipolar coupling with ^{14}N, the most shielded element is aligned with the M–CN vector. The principal values of the chemical shielding tensor are quite similar to those reported for acetonitrile, and there is relatively small variation among the three metals.

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