# Articles

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## Variable-Temperature Cross Polarization–Magic Angle Spinning $^{13}$C NMR of Crystalline $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$ and $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$. Tricarbonyl Group Rotation in the Solid State

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The variable-temperature CP-MAS $^{13}$C NMR spectra of $^{13}$CO-enriched crystalline $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$ and $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$ are reported. The results suggest that the tricarbonyl groups undergo a rotation in the solid state while the arene rings remain static. Maximum line broadening is observed for the carbonyl signals near room temperature. The carbonyl signals sharpen dramatically at high and low temperatures. An analysis of the line widths at various temperatures yields tricarbonyl group rotational energy barriers of 65 and 71 kJ/mol for the chromium and molybdenum complexes, respectively.

### Introduction

In the last 20 years, much attention has been directed toward the detection and characterization of intramolecular motions in metal carbonyl complexes using solution and solid-state NMR spectroscopy.[1-5] For many mononuclear and polynuclear metal carbonyls, the rearrangements are best described by polytopal reorganizations of the ligand polyhedron.[6-8] Thus, in iron pentacarbonyl, axial–equatorial exchange is accounted for by the Berry pseudorotation,[6] while rearrangements in the tetranuclear clusters, $M_4(CO)_{12}$, may be described by expansion of the ligand icosahedron to a cuboctahedron.[7,8] It is apparent from magic angle spinning $^{13}$C NMR results that, in the solid state, metal cluster reorientation may occur independently of ligand polyhedron expansion for clusters such as $Fe_3(CO)_{12}$[9] and $Co_4(CO)_{12}$.[10] Results from calculations are also consistent with the possibility of metal reorientation in $Co_4(CO)_{12}$.[11,12]

While there are many examples of direct intramolecular carbonyl exchange in solution that do not involve either polytopal reorganization of the ligands or metal cluster reorientation, there are no well-documented cases for carbonyl motion in the solid state. A good example is represented by $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, which in solution undergoes bridge–terminal exchange[13] but is static in the solid state.[14]

Perhaps the simplest example of intramolecular carbonyl exchange in solution is represented by rotation of a metal tricarbonyl group bonded to a larger molecule.[2] This involves a minimum of motion and may be expected to occur in the solid state also. There is ample precedent for threefold rotations in the solid state for pendant methyl groups in organic molecules.[15] These, of course, are smaller than metal tricarbonyls and would be expected to rotate much more readily.

A solution $^{13}$C NMR study[16] of monosubstituted $(\eta^6\text{-arene})Cr(CO)_3$ complexes indicates that an equilibrium exists between two conformations via a rotation about the chromium–arene bond: one in which the three carbonyl ligands are eclipsed with ring carbons 2, 4, and 6 and the other in which the carbonyl ligands are eclipsed with ring carbons 1, 3, and 5. These are shown schematically in Figure 1. Evidence for these two conformations, which are in rapid equilibrium, is given by changes in the chemical shifts of the appropriate ring carbon atoms with temperature. For $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$, the conformation in which the carbonyl groups are eclipsed with ring carbons 1, 3, and 5 is the preferred structure at 25 °C and becomes increasingly predominant at lower temperatures. Exchange between these conformations remains rapid at low temperatures. Another study dealing with substituted $(\eta^6\text{-arene})Cr(CO)_3$ complexes[17] supports these findings and further shows that in the sterically hindered complex (1,3-di-*tert*-butylbenzene)$Cr(CO)_3$ rotation about the chromium–arene bond is rapid even at a temperature of −60 °C, as evidenced by the lack of broadening of the carbonyl resonances in the $^{13}$C NMR spectra. For the related cycloheptatriene molecules, $(\eta^6\text{-}C_7H_8)Cr(CO)_3$ and $(\eta^6\text{-}C_7H_8)Mo(CO)_3$, solution $^{13}$C NMR spectroscopy indicates a broadening of the carbonyl signals at −28 and −13 °C, respectively.[18] At lower temperatures, these split into two peaks with relative areas 1:2. The peaks were assigned to the two different carbonyl ligand types present in the crystal structures of the complexes. The estimated activation energies for the motions of the hydrocarbon rings relative to the carbonyl ligands were 46 and 50 kJ/mol for the chromium and molybdenum compounds, respectively.

A study of crystalline $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ by broad-line $^1$H NMR investigated the rotation of the coordinated benzene ring in the solid state.[19] By measuring the line width of the proton signal at various temperatures, two line-narrowing regions are observed; these occur at about −165 and −45 °C. The activation energy of the motion at −165 °C is 14 ± 2 kJ/mol and is attributed

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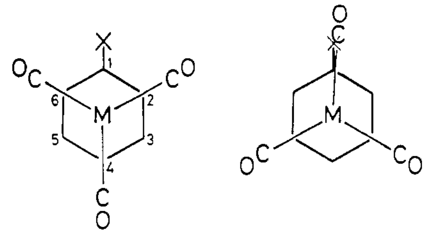

**Figure 1.** Schematic representations of the two proposed orientations of monosubstituted (arene)metal tricarbonyl complexes in solution. For $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$ the structure on the right is observed in the solid state.[28]

to a hindered ring rotation that compares favorably with the value of 18 kJ/mol measured for solid benzene.[20] The activation energy of the motion causing the line narrowing at −45 °C is estimated to be 30 ± 3 kcal/mol. However, the type of motion responsible for this further narrowing was not deduced. It was noted, though, that solid benzene is characterized by the onset of a molecular motion at a relatively high temperature (greater than −40 °C) with an activation energy of approximately 67 kJ/mol and that the two motions may be related. In solid benzene this high activation barrier process is thought to be due to rotation of benzene about axes in the plane of the molecule.[20] Ring rotations in the solid state have also been detected for coordinated cyclooctatetraene in the complexes $(\eta^4\text{-}C_8H_8)Fe(CO)_3$, $(\mu\text{-}\eta^8\text{-}C_8H_8)\text{-}Fe_2(CO)_5$, and $(\mu\text{-}\eta^8\text{-}C_8H_8)_2Ru_3(CO)_4$ by using broad-line $^1H$ NMR[21-23] and magic angle spinning $^{13}C$ NMR.[24] The corresponding activation energies are 38, 10.9, and 21.8 kJ/mol, respectively.[25] Rotation of coordinated rings is also well documented for these molecules, and others, in solution.[26] NMR spectroscopy is a powerful tool to detect motions in solids and is complementary to X-ray diffraction techniques, which may detect disorders but not dynamic processes.

In this study, we investigate metal tricarbonyl group rotation in the solid state for complexes in which arene ring rotation is unlikely. We cannot exclude the possibility of a series of pairwise exchanges of carbonyl ligands in the solid state as an alternative to rotation of the tricarbonyl group. In particular, the methyl group in toluene effectively prevents rotation in the plane of the arene ring. While the methyl group in toluene is observed to rotate in the solid state, there is no evidence for phenyl ring rotation.[27] Also the phenyl rings in solid $C_6H_5CF_3$ are immobile.[28]

## Experimental Section

**Synthesis.** Carbon-13-enriched $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$ was prepared by stirring a toluene solution of the isotopically normal complex under an atmosphere of $^{13}CO$ for 3 days. Some $Mo(CO)_6$ formed during the exchange, so it was necessary to reflux the toluene solution for an additional 20 h under nitrogen to yield the tricarbonyl complex. Enrichment of 10% in $^{13}CO$ was estimated by infrared spectroscopy.

An enriched sample of $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$ was prepared in the following manner. An acetonitrile solution of $Cr(CO)_3(CH_3CN)_3$ was stirred under an atmosphere of $^{13}CO$ for 3 days. The chromium hexacarbonyl produced was converted back to the tris(acetonitrile) complex by refluxing the solution under nitrogen. The acetonitrile was removed under vacuum to yield enriched $Cr(CO)_3(CH_3CN)_3$. This complex was then refluxed in toluene to yield the desired complex. Enrichment of 15% in $^{13}CO$ was estimated by infrared spectroscopy.

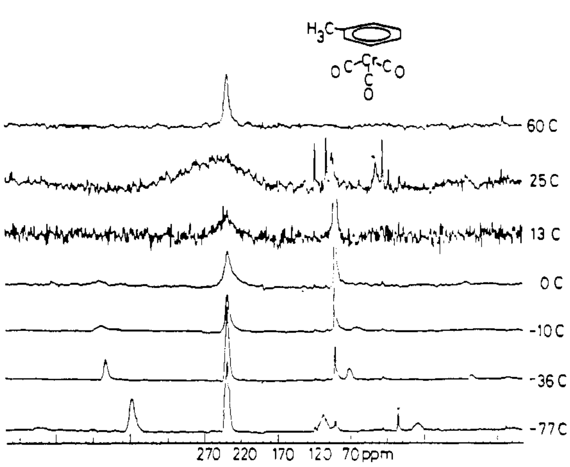

**Figure 2.** Variable-temperature CP-MAS $^{13}C$ NMR for crystalline $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$.

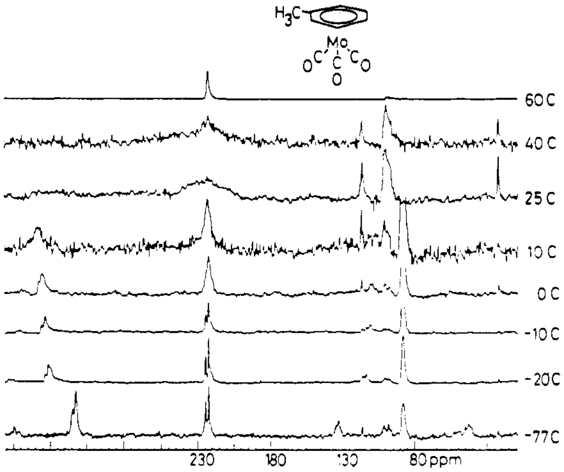

**Figure 3.** Variable-temperature CP-MAS $^{13}C$ NMR for crystalline $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$.

**NMR Measurements.** Cross polarization–magic angle spinning experiments were run with a Chemagnetics 2-T superconducting magnet and a Chemagnetics probe and variable-temperature controller interfaced to a JEOL FX60QS NMR console. The observation frequency for carbon was 22.63 MHz. The rf conversions and interfacing were done locally.

All samples were prepared under nitrogen in a Vacuum Atmospheres drybox. Delrin rotors were used for subambient temperatures, and Kel-F rotors were used for obtaining spectra above room temperature. The rotors were sealed with Plasticine in the drybox to prevent decomposition of the samples during data acquisition.

Dry nitrogen gas, from liquid-nitrogen boil-off, was used as the drive gas and bearing gas for all low-temperature work. House air was used at room temperature and above for the spinner and bearing. A thermocouple placed in the spinner airstream immediately prior to the sample was used to measure the temperature. All spectra were recorded on samples that had equilibrated for 10 min at the reported temperature. The temperatures as indicated by the thermocouple varied no more than ±3 °C during data acquisition. The Delrin rotor material yields a single resonance at 89.3 ppm; this was used as the chemical shift reference.

## Results

**$(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$.** As shown in Figure 2, a single broad resonance is observed at 25 °C in the carbonyl region of the CP-MAS $^{13}C$ NMR spectrum of $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$. The peak is centered at about 236 ppm ($Me_4Si$) and has a line width of 2140 Hz. Heating the sample to 60 °C causes the carbonyl signal to narrow to a single peak at 236 ppm with a line width of 164 Hz. Cooling the sample below 25 °C again causes a narrowing of the carbonyl signal to a single peak at 236 ppm, which continues to narrow as the temperature is lowered. The chemical shift remains constant. The peak widths and corresponding temperatures are as follows: 539 Hz at 13 °C, 195 Hz

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at 0 °C, 117 Hz at −10 °C, and 117 Hz at −36 °C. However, at −77 °C the line width increases to 180 Hz and a shoulder is present at 233 ppm. This is probably due to two different carbonyl environments within the complex (vide infra). The individual carbonyl signals are not resolvable due to their line widths and close proximity. Other features in the spectra include signals due to the ring carbons (which are most prominent at 25 °C due to the large number of scans), the signal at 89.3 ppm due to Delrin in the lower temperature spectra, and spinning sidebands that begin to appear in the −10, −36, and −77 °C spectra due to the slower spinning rates at these temperatures. The spinning rate varied from 2000 to 4000 Hz from −77 to +60 °C. No significant changes in the chemical shifts and line widths of the ring carbon signals were observed as a function of temperature.

**($\eta^6$-$C_6H_5CH_3$)Mo(CO)$_3$.** The CP-MAS $^{13}$C NMR spectra of ($\eta^6$-$C_6H_5CH_3$)Mo(CO)$_3$ are shown in Figure 3. At 25 °C, a single broad carbonyl resonance is observed at 224 ppm with a line width of 684 Hz. When the spectrum is recorded at 40 °C, the carbonyl peak narrows to 200 Hz, and at 60 °C it narrows further to 31 Hz. Also, as the sample is cooled to 10 °C, the peak sharpens to a single resonance at 224 ppm with a line width of 94 Hz. However, at −10 °C two overlapping singles are present at 226 and 223 ppm, both having a line width of 21.5 Hz. At −20 °C the resonances sharpen to 15.6 Hz and are well resolved. The relative intensities of the peaks at 226 and 223 ppm are approximately 1:2. This is attributable to two different types of carbon monoxide ligands present in different chemical environments within the molecule. Spinning sidebands are evident in the lower temperature spectra as is the Delrin signal at 89.3 ppm. The signals due to the ring carbons are also observed but do not demonstrate any chemical shift or line width changes at different temperatures.

## Discussion

The NMR data for ($\eta^6$-$C_6H_5CH_3$)M(CO)$_3$ (M = Cr, Mo) shown in Figures 2 and 3 show two distinct line-broadening regimes. This is most easily seen in the data for the molybdenum compound in Figure 3. From −77 to 0 °C, the signals due to two different carbonyl environments collapse into a single broad line. This broadens slightly from 0 to 10 °C and broadens extensively at room temperature. The low-temperature line-broadening regime is easily explained by exchange of carbonyl ligands between the two different environments present in the molecule. This represents typical solution-like behavior for a fluxional process. The high-temperature line broadening is more complicated but is probably due to the same motional process responsible for carbonyl exchange.

The temperature dependence of CP-MAS NMR line widths has been previously discussed by Rothwell and Waugh.[29] The relationship they derived is applicable to a system where $^{13}$C spins are coupled to $^1$H spins though dipole-dipole interactions where the protons are subjected to an rf decoupling of intensity $\omega_1$. The spins are assumed to possess a rotational motion with a correlation time $\tau_c$. For this type of system, two $^{13}$C NMR line-narrowing regions are predicted: one at $\omega_1\tau_c \ll 1$ (short correlation limit) and the other at $\omega_1\tau_c \gg 1$ (long correlation limit). The point of maximum broadening occurs at $\omega_1\tau_c = 1$. Using CP-MAS $^{13}$C NMR, Rothwell and Waugh have illustrated this behavior for a number of hydrocarbon compounds that possess rotational motions in the solid state.[29a] These compounds, e.g. adamantane and hexamethylbenzene, undergo solid-state rotations; however, they do not exchange carbons with different environments. Thus, these are not fluxional molecules.

Although the line shape behavior for molecular motions in the solid state appear unusual compared to typical solution behavior where rapid molecular tumbling leads to line narrowing only, activation parameters are extracted in a way that is completely familiar. Since the line width, $\Delta$, is a function of $\tau_c$, an Arrhenius plot of log $\Delta$ vs. $1/T$ yields an activation energy.

Our results indicate that the aromatic rings in both the chromium and the molybdenum compounds are static in the solid state since the line widths due to the ring carbons do not vary as the temperature (and hence the correlation times for any rotational motions) is changed. Furthermore, the chemical shifts remain unchanged, which indicates that only one rotational conformation is present in the solid state. This is consistent with the X-ray structure determined for ($\eta^6$-$C_6H_5CH_3$)Cr(CO)$_3$.[30] However at 25 °C, the broadness of the carbonyl signals for both complexes is consistent with a rotational motion of the tricarbonyl group, the rate of which is near the point of maximum line broadening, i.e. $\omega_1\tau_c \approx 1$. As the samples are heated to 60 °C, the line widths narrow as the correlation times decrease so that the rates of the rotational motions for the two complexes approach the short correlation limit where $\omega_1\tau_c < 1$. The long correlation limit for the rotational motions of the tricarbonyl groups is neared as the samples are cooled, and the correlation times increase so that $\omega_1\tau_c > 1$, as evidenced by a narrow line for the carbonyls at 10 °C for ($\eta^6$-$C_6H_5CH_3$)Mo(CO)$_3$. At even lower temperatures, the rotational motion is sufficiently slow so that the distinct carbonyl ligands present in different chemical environments within the complexes are distinguishable by NMR. This is particularly evident for the molybdenum compound (Figure 3) and accounts for the shoulder in the −77 °C spectrum of ($\eta^6$-$C_6H_5CH_3$)Cr(CO)$_3$.

The crystal structure of ($\eta^6$-$C_6H_5CH_3$)Cr(CO)$_3$ has been determined by X-ray crystallography;[30] however, there is no report of a structure for its molybdenum analogue. The chromium complex lies on a general position in the lattice and thus has no crystallographically imposed symmetry. The molecular parameters are consistent with near mirror plane symmetry with the carbonyl ligands nearly eclipsed with respect to ring carbons 1, 3, and 5[30] (see Figure 1). The average deviation from a perfectly eclipsed structure is 2.2°. It is likely that the molybdenum complex has a similar structure in the solid state. The thermal ellipsoids for the chromium complex show a small oscillation about the pseudo-threefold axis, but there is no evidence for different orientations of the toluene ring.

Thus the peak at 226 ppm is assignable to the carbonyl ligand that is eclipsed with respect to the methyl group of the aromatic ring. The peak at 223 ppm would then be assigned to the other two carbonyl ligands if it is assumed that they have degenerate chemical shifts. This assignment is supported by the relative peak areas, 1:2, and the fact that the weighted average of the chemical shifts yields the value of 224 ppm observed at temperatures above the coalescence point.

The activation barrier may be estimated either by line shape analysis of the two-site exchange process in the low-temperature line-broadening regime or by relating line widths to exchange rates in the short correlation time regime in the manner of Rothwell and Waugh.[29] Only the spectra for the molybdenum complex are of sufficient quality to simulate for a two-site exchange. This analysis yields an activation energy of 71 kJ/mol. In the short correlation limit (temperatures above 30 °C) an activation barrier of 75 kJ/mol is estimated. The agreement of these numbers (within 4 kJ/mol) is good evidence that both line-broadening regimes are due to the same phenomenon, namely rotation of the tricarbonyl group. In a similar fashion, in the short correlation limit an activation barrier of 65 kJ/mol is estimated for rotation of the −Cr(CO)$_3$ group in ($\eta^6$-$C_6H_5CH_3$)Cr(CO)$_3$.

As expected, the activation barriers for tricarbonyl rotation in the solid state are significantly higher than for similar motions in solution. Also, it is evident that the methyl group of the

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$$\frac{1}{T_2} = \frac{4\gamma_I^2\gamma_s^2\hbar^2}{15r^6}I(I+1)\tau_c, \quad \omega_1\tau_c \ll 1$$

and in the long correlation limit

$$\frac{1}{T_2} = \frac{4\gamma_I^2\gamma_s^2\hbar^2}{15r^6}I(I+1)\frac{1}{\omega_1^2\tau_c}, \quad \omega_1\tau_c \gg 1$$

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coordinated toluene ring effectively eliminates rotation of the arene ring, and therefore the observed line shape changes are due to rotation of the $M(CO)_3$ group. It should be noted that not all tricarbonyl groups show evidence for dynamic behavior in the solid state. For example, $Mo(CO)_3(CH_3CN)_3$ does not show any change in line width from −60 to +60 °C. Thus, in this temperature range the relationship $\omega_1\tau_c = 1$ is not satisfied. It is likely that this molecule is static in the solid state.

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**Registry No.** ($\eta^6$-$C_6H_5CH_3$)$Cr(CO)_3$, 12083-24-8; ($\eta^6$-$C_6H_5CH_3$)$Mo(CO)_3$, 12083-34-0.

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# Applications of $^{95}$Mo NMR Spectroscopy. 17.[1] $^{95}$Mo and $^{14}$N Relaxation Time Measurements Confirming That $[Mo(CN)_8]^{4-}$ Is Dodecahedral in Aqueous Solution

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Variable-temperature NMR line width measurements of $^{95}$Mo and $^{14}$N in aqueous solutions of $K_4[Mo(CN)_8]\cdot 2H_2O$ indicate that the stereochemistry of the $[Mo(CN)_8]^{4-}$ ion in solution is dodecahedral. A value for the $^{95}$Mo quadrupole coupling constant of 3.61 MHz is obtained.

## Introduction

Although it has been nearly 50 years since Hoard[3] reported that $K_4[Mo(CN)_8]\cdot 2H_2O$ contained an eight-coordinate anion, $[Mo(CN)_8]^{4-}$, of dodecahedral geometry, its stereochemistry in solution remains the subject of debate.[4] It is apparent[5] that the dodecahedral ($D_{2d}$) and square-antiprismatic ($D_{4d}$) arrangements are of similar energies and that both are more stable than the cube ($O_h$). Solvation or crystal-packing energies can determine which geometry is adopted. Indeed, the anion in $Cd_2[Mo(CN)_8]\cdot 2N_2H_4\cdot 4H_2O$ is square antiprismatic.[6]

While interpretation of earlier vibrational studies[7] in aqueous solution was confusing, definitive Raman data[8] favored the $D_{2d}$ structure. The $^{13}$C NMR spectrum[9] shows a single resonance indicative of equivalent CN ligands. This was interpreted in terms of the $D_{2d}$ structure undergoing an intramolecular rearrangement, via the $D_{4d}$ structure, which was fast on the $^{13}$C NMR time scale.

Line widths of quadrupolar nuclei such as $^{95}$Mo and $^{14}$N are related to the quadrupolar relaxation time, the electric field gradient term ($q_{zz}$) within the quadrupole coupling constant, and the rotational correlation time $\tau_c$ by[10]

$$\pi W_{1/2} = T_{2Q}^{-1} = T_{1Q}^{-1} = \frac{3\pi^2}{10}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(\frac{e^2q_{zz}Q}{h}\right)^2\left(\frac{1+\eta^2}{3}\right)\tau_c \quad (1)$$

Table I. Temperature Dependence of $^{95}$Mo and $^{14}$N NMR Line Widths for Aqueous $K_4[Mo(CN)_8]\cdot 2H_2O$ (0.3 M)

| $t$, °C | line width, Hz[a] |  | $t$, °C | line width, Hz[a] |  |
|---|---|---|---|---|---|
|  | $^{95}$Mo | $^{14}$N |  | $^{95}$Mo | $^{14}$N |
| 18 | 72 | 1165 | 75 | 32 | 461 |
| 39 | 52 | 773 | 90 | 30 | 394 |
| 53 | 42 | 620 | 97 | 29 | 364 |
| 64 | 37 | 535 |  |  |  |

[a] Line widths have been corrected for 2-Hz inhomogeneity broadening.

In one of the early reports of $^{95}$Mo NMR,[11] the line width of aqueous $K_4[Mo(CN)_8]\cdot 2H_2O$ was found to be 75 Hz. Given that compounds of high symmetry (e.g., $[Mo(CO)_6]$, $[MoO_4]^{2-}$, and *fac*-$[Mo(CO)_3(py)_3]$ for which the electric field gradient is zero, ideally) have intrinsic line widths <2 Hz, the authors noted that the observed line width for $[Mo(CN)_8]^{4-}$ is inconsistent with a cubic stereochemistry. It is also inconsistent with the $D_{4d}$ structure, but not with the $D_{2d}$ structure, which should exhibit a nonzero electric field gradient.[12] A comparison of the line width of $[Mo(CN)_8]^{4-}$ with those of other structures given in our earlier studies of $^{95}$Mo relaxation times[10] shows it to be comparable with lower symmetry structures.

Since $^{95}$Mo line widths of complexes where the $^{14}$N atom is directly bound to the molybdenum show no scalar coupling effects,[13] they are unlikely to contribute to the $^{95}$Mo line width in the present case. Therefore, the observed $^{95}$Mo line width of this complex in solution appears to be consistent with quadrupolar relaxation involving tumbling of the $[Mo(CN)_8]^{4-}$ ion with $D_{2d}$ symmetry in solution. However, the possibility also exists that relaxation is quadrupolar but with fluctuation of the EFG being dependent on interconversion of sets of nonequivalent ligands (as proposed from the $^{13}$C NMR study[9]), rather than on rotational reorientation of the anion.

$^{95}$Mo inversion-recovery $T_1$ and $^{95}$Mo and $^{14}$N line width measurements in the temperature range 18–97 °C are reported

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