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.** $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3$, 12083-24-8; $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$, 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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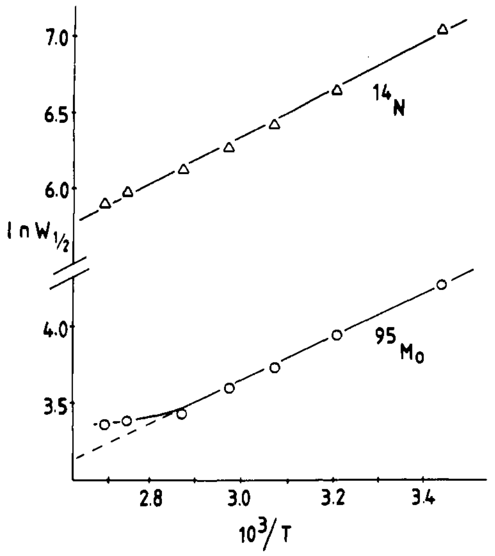

**Figure 1.** $^{95}$Mo and $^{14}$N line width temperature dependence for 0.3 M aqueous $K_4[Mo(CN)_8]\cdot 2H_2O$.

here and are consistent with quadrupole relaxation of a dodecahedral ($D_{2d}$) $[Mo(CN)_8]^{4-}$ anion tumbling in solution.

## Experimental Section

NMR measurements of a 0.3 M aqueous solution of $K_4[Mo(CN)_8]\cdot 2H_2O$ in a 10-mm sample tube were carried out on a JEOL FX-200 spectrometer at 13.0 MHz for $^{95}$Mo and 14.4 MHz for $^{14}$N. Spectra were recorded without sample spinning or locking. The $^{13}$C spectrum measured at 50 MHz showed a single sharp line. Further details may be found in an earlier report.[10]

## Results and Discussion

Results of variable-temperature measurements of $^{95}$Mo and $^{14}$N line widths in 0.3 M aqueous solutions of $K_4[Mo(CN)_8]\cdot 2H_2O$ are presented in Table I and Figure 1. The $^{95}$Mo and $^{14}$N line widths over the temperature range 18–97 °C decreased from 72 to 29 Hz and 1165 to 364 Hz, respectively. The decrease in line widths with increasing temperature is characteristic of quadrupolar relaxation, but not of chemical exchange or scalar coupling effects. The line width of 72 Hz at 18 °C can be compared to 75 Hz measured previously.[11] In addition, we have reported[10] $^{95}$Mo $T_1$ and $T_2$ values. The inversion-recovery $T_1$ value of 4.45 ms converts to a natural line width of 72 Hz. The equality of the $T_1$ and $T_2$ values is also inconsistent with scalar coupling or chemical exchange line width contributions.

Since ion-pairing effects on the electric field gradient have been shown to be unimportant in $[Co(CN)_6]^{3-}$,[14,15] and other Co$^{III}$ complexes[16,17] that have $O_h$ symmetry and therefore a small intrinsic electric field gradient, they are unlikely to be important here. The $^{95}$Mo line widths and relaxation times are consistent with quadrupolar relaxation of a dodecahedral complex, having a nonzero electric field gradient, which undergoes reorientation with rotation of the complex or which fluctuates due to rapid intramolecular exchange[9] between nonequivalent sets of ligands. Since the correlation times associated with these different physical processes and their temperature dependence will be different, they can be distinguished by variable-temperature line width measurements for $^{95}$Mo in parallel with those of the $^{14}$N nucleus.

The value of the $^{14}$N quadrupole coupling constant will not be affected by interchange of ligand sets, since the major contribution to the electric field gradient comes from the carbon–nitrogen triple bond and is not greatly different over a range of crystal structures.[14,18,19] The $^{14}$N quadrupole coupling constants for a number of metal cyano complexes have been measured by NQR[19] and are in the range 3.47–4.20 MHz. Employing eq 1, Ader and Loewenstein[14] used an estimate of 3.68 MHz for $K_3[Co(CN)_6]$ and the $^{14}$N NMR line width to derive a rotational correlation time $\tau_c$ = 18 ps for $[Co(CN)_6]^{3-}$ in aqueous solution at room temperature. A value of 15 ps at 32 °C was obtained in a similar manner.[18] The same estimate and a peak-to-peak line width from the derivative of the $^{14}$N NMR signal led[20] to $\tau_c$, 22 ps, for aqueous $K_4[Mo(CN)_8]\cdot 2H_2O$.

A $^{14}$N quadrupole coupling constant of 3.68 MHz and a $^{14}$N line width of 1165 Hz (Table I) lead to $\tau_c$, 18.3 ps at 18 °C. The Gierer–Wirtz model[21] estimates $\tau_c$ as 25 ps using a solute radius for $[Mo(CN)_8]^{4-}$ of 4.87 Å (average Mo–N distance 3.315 Å,[7] plus a nitrogen van der Waals radius of 1.55 Å) and a solvent radius for $H_2O$ of 3.63 Å.[22] It is apparent that the $^{14}$N NMR line width observed for $[Mo(CN)_8]^{4-}$ is consistent with the rotational correlation time predicted for this anion.

Arrhenius plots (Figure 1) are linear below 75 °C for both the $^{95}$Mo and $^{14}$N nuclei. The derived activation energies of 11.8 and 12.9 kJ mol$^{-1}$ are the same within experimental error, as would be expected if both line widths are controlled by rotation of $[Mo(CN)_8]^{4-}$. The observations and the substantial $^{95}$Mo NMR line width are consistent with dodecahedral ($D_{2d}$) stereochemistry in aqueous solution.

Using $\tau_c$, 18.3 ps, and $^{95}$Mo $T_1$, 4.45 ms, eq 1 provides a $^{95}$Mo quadrupole coupling constant of 3.61 MHz. This is much larger than those derived for high-symmetry complexes such as $[Mo(CO)_6]$, 0.133 MHz,[23] or $[Mo(CO)_3(\eta\text{-arene})]$, 1.0–1.4 MHz,[24] but is similar to that of $[Mo(CO)_5(SbPh_3)]$, 3.75 MHz.[25] A substantial electric field gradient seems to be associated with the dodecahedral structure of the $[Mo(CN)_8]^{4-}$ ion in aqueous solution.

Fortuitously, the quadrupole coupling constants for $^{95}$Mo and $^{14}$N in $[Mo(CN)_8]^{4-}$ are very similar. The large differences in line widths with relaxation times result entirely from the difference in the spin term, $(2I + 3)/I^2(2I - 1)$ of eq 1, which has a value of $^8/_{25}$ for $^{95}$Mo and 5 for $^{14}$N.

The Arrhenius plot (Figure 1) for $^{95}$Mo deviates from linearity as the boiling point of the solvent is approached. This is not observed for $^{14}$N. This observation is not necessarily due to a change in the operation of the quadrupolar mechanism, since the observed temperature dependence is consistent with a contribution to the relaxation rate by the spin rotation mechanism. Spin rotation relaxation can be very efficient for nuclei with large chemical shift ranges and becomes increasingly efficient as the temperature and angular momentum correlation time $\tau_j$ increases. It has been suggested as a possible $^{59}$Co NMR relaxation mechanism in octahedral Co$^{III}$ complexes,[26] including $[Co(CN)_6]^{3-}$,[14] and is the dominant ESR relaxation mechanism in $K_3[Mo(CN)_8]$.[20]

The difference between the observed $^{95}$Mo line width and the extrapolated quadrupolar line width at 97 °C could be accounted for by a spin rotation contribution to the total relaxation rate of 12 s$^{-1}$, or a $T_1$ of 80 ms. These are not unreasonable values for the spin rotation mechanism under these conditions.[27]

The chemical shift range for $^{14}$N is only 1000 ppm compared with 7000 ppm for $^{95}$Mo, and the $^{14}$N quadrupolar relaxation rate in $[Mo(CN)_8]^{4-}$ is 15 times larger than that of $^{95}$Mo. Therefore, spin rotation would not be expected to make a significant con-

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tribution to the $^{14}N$ line width, even at high temperatures, consistent with the Arrhenius plot for $^{14}N$ being linear over the entire temperature range (Figure 1).

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**Registry No.** $K_4[Mo(CN)_8]$, 17456-18-7.

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# Synthesis of Tetraethylammonium Dithionite and Its Dissociation to the Sulfur Dioxide Radical Anion in Organic Solvents†

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The facile synthesis of $[Et_4N]_2[S_2O_4]$ from $Na_2S_2O_4$ and $[Et_4N]OH$ has been carried out by using anion-exchange chromatography on Bio-Rex 5. This form of dithionite is soluble in organic solvents, allowing its ability as a reducing agent to be utilized in nonaqueous media. Electronic and EPR spectral studies have shown that the $[S_2O_4]^{2-}$ ion is extensively dissociated to the sulfur dioxide radical anion in the organic solvents dimethylformamide, dimethyl sulfoxide, and acetonitrile, complementing some,[28] and conflicting with other,[27] previous studies dealing with the electrochemical generation of $[SO_2]^-$ from sulfur dioxide in organic solvents. In general, the equilibrium constants for the formation of $[SO_2]^-$ from $[S_2O_4]^{2-}$ in these nonaqueous solvents (DMF, 42.4 mM; $Me_2SO$, 11.3 mM; MeCN, ca. 40 mM) are $10^7$ times greater than in aqueous media ($1.4 \times 10^{-6}$ mM).[3] The dissociation to the radical anion in nonaqueous media is very dependent on the water content of the solvent, an effect that has been quantitated for the $DMF/H_2O$ system. These findings suggest that $[S_2O_4]^{2-}$ is preferentially stabilized by solvents of higher polarity or perhaps by $H_2O$ only. Solid-state EPR studies also indicate that the isolated solid $[Et_4N]_2[S_2O_4]$ contains significant, but small (ca. 1%), amounts of $[Et_4N][SO_2]$.

The dithionite ion ($[S_2O_4]^{2-}$) is a ubiquitous reducing agent that has been used both in relatively small scale organic synthetic procedures[1] and in larger amounts as a bleach in commercial vat dyeing.[2] However, $[S_2O_4]^{2-}$ has perhaps been most widely employed in biochemical systems, where it has been used for the in vitro reduction of enzymes and other redox-active proteins such as ferredoxins and/or as an agent for removal of dissolved oxygen from aqueous solutions used in anaerobic biochemical procedures. Although $[S_2O_4]^{2-}$ itself is occasionally important as an actual reductant, numerous kinetic studies involving metalloproteins,[3-10] synthetic transition-metal complexes,[11-13] organic dyes,[14] and simple inorganic species[15] have shown that usually the sulfur dioxide radical anion, $[SO_2]^-$, formed from dissociation of $[S_2O_4]^{2-}$, is the active species in "dithionite reductions" even though it is present in only small amounts.

Virtually all of the above studies have been carried out in *aqueous solution* on the disodium salt of dithionite, by far the most commonly available and employed form of the reducing agent. By contrast, there is much less information on the properties of the dithionite ion in *nonaqueous solution*, most likely due to the fact that $Na_2S_2O_4$ is effectively insoluble in most organic solvents. Herein we report a detailed, refined method for the preparation of $[Et_4N]_2[S_2O_4]$ and present EPR and electronic spectroscopic data that have been used to quantitate the dissociation of dithionite to the sulfur dioxide radical anion in *N,N*-dimethylformamide (DMF), acetonitrile (MeCN), and dimethyl sulfoxide ($Me_2SO$).

## Experimental Section

**Materials and Methods.** All operations were carried out in the absence of oxygen by using Schlenk tube techniques, glovebox manipulation, or anaerobic chromatographic apparatus and solvents that were degassed prior to use. DMF and MeCN were both vacuum-distilled from $CaH_2$ (the former at reduced pressure) before use. $Me_2SO$ was used as received from Burdick and Jackson. Commercial pH 10 borate buffer was from VWR. Electronic spectra were obtained on a Cary 118C instrument, IR spectra on a Beckman IR-20A spectrophotometer, and EPR spectra on a spectrometer system that has been described previously.[16] Bio-Rex 5 anion-exchange resin (200–400 mesh) was purchased from Bio-Rad Laboratories.

**Purification of Sodium Dithionite.** A variation of the literature procedure[17] was used. Commercial $Na_2S_2O_4$ from a variety of sources (10 g) was dissolved in 0.02 M NaOH (55 mL) and an additional 0.40 mL of 3 M NaOH added. This solution was filtered, the filtrate was heated to 65 °C, and MeOH (75 mL) was slowly added. The white granular product was isolated by filtration, washed with hot MeOH, and dried under vacuum. Recovery was typically 60–70%. Repeated reprecipitation gave solids up to 90% pure on the basis of a comparison of their UV spectra with literature[18] values ($\lambda_{max} = 313$ nm; $\epsilon = 8000\ M^{-1}\ cm^{-1}$).

**Preparation of $[Et_4N]_2[S_2O]$.** A column (2.5 cm in a diameter and 1.5 cm long) of Bio-Rex 5 anion-exchange resin in the $Cl^-$ form was made anaerobic by elution of 300 mL of rigorously degassed $H_2O$. The column was converted to its dithionite form by slow elution of a solution of purified $Na_2S_2O_4$ (9.0 g; 51.7 mM) in $H_2O$ (60 mL) and was then washed with $H_2O$ until the eluant showed no capacity to reduce methylviologen. This resin was treated with 0.5 M $[Et_4N][OH]$ in $H_2O$ and the pH of the eluant carefully monitored. At the first sign of a rise in pH, the elution was discontinued and the eluant evaporated to dryness under vacuum at 30 °C to give an oily, pale yellow residue. This material was then heated for an additional 6 h at 70–80 °C under high vacuum causing both solidification to a well-formed product and a color change to brighter yellow. Reprecipitation of this solid from DMF did not significantly alter its purity as evidenced by both elemental analytical and

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† Contribution No. 913.

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