Determination of the Structures of the Octacyanomolybdate(IV) and Octacyanotungstate(IV) Ions in Aqueous Solution Utilizing Laser–Raman Depolarization Ratios

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Abstract: The laser–Raman spectra of crystalline $K_4Mo(CN)_8 \cdot 2H_2O$ and $K_4W(CN)_8 \cdot 2H_2O$ and aqueous solutions of these materials are reported. Accurate values for the depolarization ratios of the aqueous-solution Raman shifts are measured, and the number of fully symmetric modes exceeds that allowed for a square-antiprismatic geometry for these complex ions. Also, in the low-frequency region (500–200 cm^{-1}), the spectra of the solutions and the corresponding solids are identical. Retention of the dodecahedral structure determined for the crystalline materials upon dissolution is indicated, in contrast to the conclusion, drawn from earlier vibration investigations, that conversion to a D_{4d} structure occurs.

Three decades separate the initial investigation by Hoard and Nordsieck[1] of the stereochemistry of the octacyanomolybdate(IV) ion, rightfully regarded as "the classic chemical exemplar of eight coordination,"[2] and the reexamination of this structure utilizing three-dimensional X-ray techniques by Hoard, Hamor, and Glick.[3] The proliferation of structural determinations of discretely octacoordinate species during this period witnesses the frequent occurrence of complexes exhibiting dodecahedral or square-antiprismatic geometries.[4] Although these approximately equi-energetic polyhedra are the most stable stereochemical configurations for eight-coordinate transition metal complexes,[2] experimental evidence has but adumbrated the relative importance of a number of factors (ligand–ligand repulsions, multidentate ligand constraints, crystal energy, or solvation effects)[2] in establishing the superiority of one of the two forms for a particular compound, and the aforementioned structural refinement[3] was directed to clarification of this question.

In a singular experiment, Stammreich and Sala[5] employed long-wavelength helium excitation and photographic recording techniques to obtain the Raman spectrum of $Mo(CN)_8{}^{4-}$ in aqueous solution. On the basis of this spectrum it was suggested that the free ion adopts a square-antiprismatic geometry of D_{4d} point symmetry.[5] Incontrovertibly, the octacyanomolybdate(IV) ion conforms approximately to dodecahedral (D_{2d}) symmetry in solid $K_4Mo(CN)_8 \cdot 2H_2O$;[1–3] but subsequent investigations by a variety of physical methods[6] evince the interest stirred by the Raman measurements, which may be interpreted as indicating stereochemical conversion on dissolution. Indeed, while our studies were in progress, two manuscripts reporting the laser–Raman spectra of $Mo(CN)_8{}^{4-}$ and $W(CN)_8{}^{4-}$ in solid and solution phases appeared that adhere to this position.[7,8] The aqueous-solution spectra of octacyanomolybdate(IV) reported in those studies[7,8] are apparently less complete than that of the original inquiry,[5] and accurate polarization measurements are not presented. We have measured the laser–Raman spectra of $K_4Mo(CN)_8 \cdot 2H_2O$ and $K_4W(CN)_8 \cdot 2H_2O$ in the solid state and in aqueous solution. While the solid-state spectra agree with those recently recorded,[7,8] the solution data conform more closely to those of Stammreich and Sala,[5] though somewhat greater detail is evident. Moreover, it has been possible to determine accurately the polarization properties of the Raman shifts. These measurements show that the dodecahedral geometry exhibited by the anions in the solid phase[1,3,9] *is maintained* in an aqueous environment.

Experimental Section

Preparation of Compounds. $K_4Mo(CN)_8 \cdot 2H_2O$ was obtained as brilliant yellow crystals according to the procedure recommended by Furman and Miller.[10] Repeated recrystallization produced a material that analyzed at 99.62% purity by standard cerium sulfate titration, and the infrared spectrum of this material exhibited no infrared absorptions characteristic of impurities.[7]

$K_4W(CN)_8 \cdot 2H_2O$, similar in appearance to the corresponding Mo(IV) salt, was prepared according to the method suggested by Heintz,[11] and the infrared spectrum of the recrystallized material again agreed with that previously published.[7]

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(1) J. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.*, **61**, 2853 (1939).

(2) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

(3) J. L. Hoard, T. A. Hamor, and M. D. Glick, *J. Amer. Chem. Soc.*, **90**, 3177 (1968).

(4) For a superb review devoted exclusively to the chemistry of discrete eight-coordination, see: S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).

(5) H. Stammreich and O. Sala, *Z. Electrochem.*, **64**, 741 (1960); **65**, 149 (1961).

(6) (a) Electronic spectra: E. König, *Theor. Chim. Acta*, **1**, 23 (1962); R. M. Golding and A. Carrington, *Mol. Phys.*, **5**, 377 (1962); J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Amer. Chem. Soc.*, **85**, 249 (1963). (b) Electron paramagnetic resonance spectra: B. R. McGarvey, *Inorg. Chem.*, **5**, 476 (1966); R. G. Hayes, *J. Chem. Phys.*, **44**, 2210 (1966). (c) ^{13}C nuclear magnetic resonance spectra: E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965). (d) Infrared spectra: V. Lorenzelli and P. Delorme, *Spectrochim. Acta*, **19**, 2033 (1963); S. F. A. Kettle and R. V. Parish, *ibid.*, **21**, 1087 (1965); R. V. Parish, *ibid.*, **22**, 1191 (1965); (spectrum of $W(CN)_8{}^{4-}$). Earlier papers include: G. B. Bonino and G. Fabbri, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **20**, 566 (1966); E. G. Brame, Jr., F. A. Johnson, E. M. Larsen, and V. W. Meloche, *J. Inorg. Nucl. Chem.*, **6**, 99 (1958); A. Hidalgo and J. P. Mathieu, *C. R. Acad. Sci.*, **249**, 233 (1959).

(7) K. O. Hartman and F. A. Miller, *Spectrochim. Acta, Part A*, **24**, 669 (1968).

(8) R. V. Parish, P. G. Simms, M. A. Wells, and L. A. Woodward, *J. Chem. Soc. A*, 2882 (1968).

(9) H. Baadsgaard and W. D. Treadwell, *Helv. Chim. Acta*, **38**, 1669 (1955).

(10) N. H. Furman and C. O. Miller, *Inorg. Syn.*, **3**, 160 (1959).

(11) E. A. Heintz, *ibid.*, **7**, 142 (1963).

Table I. Vibrational Spectra of $K_4Mo(CN)_8 \cdot 2H_2O$ in the CN Stretching Region

Crystalline		Aqueous-solution Raman			
Raman (this study)	Infrared (ref 7)	This study	Ref 5	Ref 7	Ref 8
2135 vs[a,b]	2137 w	2134 vs, p (0.0)[c]	2135 s, p	2136 vs, p	2135 s
2129 m	2129 vs				
2128 m	2127 ?, vw, sh				
2123 mw	2124 vs				
		2119 ms, p (0.47)	2121 m	2118.5 s, dp?	2120 m
2115 s	2115 ?, vvw	} p (0.54)			
		2109 w, dp (0.71)	2114 w, sh		
2105 vs	2106 s, sh				
2102 m	2103 vvs				

[a] All frequencies in this and the following tables in cm^{-1}. [b] Abbreviations used in the tables: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad; p, polarized; dp, depolarized. [c] Values of ρ, the depolarization ratio, are given in parentheses.

Vibrational Measurements. Infrared spectra of Nujol mulls of both salts supported on CsI plates were recorded from 4000 to 200 cm^{-1} on a carefully calibrated, air-dried Perkin-Elmer Model 621 grating infrared spectrometer. Scale expansion was used to study regions of characteristic absorptions, and the recorded frequencies, accurate to ± 1 cm^{-1}, agreed with those measured by Hartman and Miller.[7] The spectrum of a cooled (*ca.* 0°), concentrated aqueous solution of the molybdenum salt was also measured using KRS-5 cells.

The laser–Raman spectra were measured on a modular instrument that has as its major components a Spex Model 1400-II double monochromator, a Spectra-Physics Model 112 helium–neon laser (monitored power level at 632.8 nm, 43 mw), an ITT–FW-130 photomultiplier with an S-20 coating, and a dc amplifier. An instrumental frequency calibration was effected using certain neon lines and known frequencies for CCl_4, CH_2Cl_2, and CH_3NO_2. The spectra of both solids and solutions were measured at a variety of spectral resolutions from *ca.* 1 to 6 cm^{-1}. The spectra of the solid materials were obtained from multicrystalline pressed pellets mounted on a goniometer head at an angle of 20° to the incident laser beam. The solutions were carefully filtered through Millipore "Solvinert" filters directly into a 1.0-ml standard Spex cell with plane windows. The reported Raman frequencies for the solid materials in the CN stretching region are accurate to better than ± 2 cm^{-1}, while an accuracy within ± 5 cm^{-1} is anticipated for other spectral regions and for the spectra of the aqueous solutions.

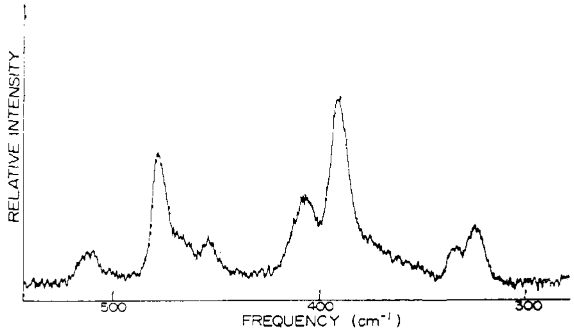

Figure 1. The partial laser-Raman spectrum (550–300 cm^{-1}) of $K_4Mo(CN)_8 \cdot 2H_2O$: slits, 5 cm^{-1}; scan rate, 20 cm^{-1} min^{-1}; time constant, 0.3 sec.

The depolarization data represent the results of multiple sets of measurements on each peak (at least five in each polarization mode). Plane-polarized incident radiation was used with subsequent analysis of the scattered light through rotation of a Polaroid film, and a polarization scrambler was placed between the Polaroid analyzer and the entrance slit of the spectrometer. The depolarization ratio, ρ, of a Raman shift is defined by the equation

$$\rho = \frac{I_\perp(\text{obsd}_\perp)}{I_\parallel(\text{obsd}_\perp)}$$

in which $I_\perp(\text{obsd}_\perp)$ is the integrated intensity of the scattered light whose polarization is perpendicular to the polarization of the incident radiation and which is observed at a 90° angle to the plane of polarization of the incident radiation and $I_\parallel(\text{obsd}_\perp)$ is the integrated intensity of the scattered light with a polarization parallel to that of the incident radiation which is observed in the same direction.[12] Thus, a depolarized line, which would be associated with a nontotally symmetrical vibration, should exhibit a depolarization ratio of 0.75, while a polarized line, which would arise from a vibrational motion possessing the full symmetry of the molecule, could have *any* value for the depolarization ratio less than 0.75 ($0 \leq \rho < {}^3/_4$). Special care was taken that significant photochemical decomposition did not occur during the period of the measurement, and changes in the number or intensities of the Raman bands were not observed. The error in these measurements, chiefly from curve resolution uncertainties, is estimated to be less than 10%.

Results

The Raman spectra of crystalline $K_4Mo(CN)_8 \cdot 2H_2O$ and $K_4W(CN)_8 \cdot 2H_2O$ are tabulated in Tables I, II, III, and IV, respectively. These spectra agree with those reported by Hartman and Miller[7] to 1 cm^{-1}, with the exception of the $W(CN)_8{}^{4-}$ band at 466 cm^{-1} that was not detected in the previous study and a reproducible splitting of the peak at 2129–2128 cm^{-1} in the spectrum of the Mo(IV) compound that we were able to resolve. The line at 466 cm^{-1} apparently corresponds to an infrared absorption at 469 cm^{-1}.[7] A portion of the low-frequency Raman spectrum of the $K_4Mo(CN)_8 \cdot 2H_2O$ solid is displayed in Figure 1, and the spectrum of this compound in the CN stretching region (*ca.* 2100 cm^{-1}) is not sufficiently different from that of $K_4W(CN)_8 \cdot 2H_2O$ in the earlier study[7] to warrant reproduction. The infrared spectra of the hydrated crystals reported in that investigation[7] are also included in Tables I–IV. To facilitate comparison, Tables I and II contain our laser–Raman spectrum of a $Mo(CN)_8{}^{4-}$ solution as well as those measured in the three previous studies. The spectra of aqueous $W(CN)_8{}^{4-}$ recorded by Hartman and Miller[7] and Parish, *et al.*,[8] are tabulated in Tables II and IV along with the data from the present investigation. The results of our polarization measurements are also presented.

The spectrum of the octacyanomolybdate(IV) ion in aqueous solution is shown in Figures 2 and 3. The upper portion of each of these figures contains the most intense polarized component of the scattered radi-

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(12) The notation is that developed in E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, pp 45–53.

Table II. Vibrational Spectra of $K_4Mo(CN)_8 \cdot 2H_2O$ in the Region 550–100 cm^{-1} [a]

Crystalline		Aqueous-solution Raman			
Raman (this study)	Infrared (ref 7)	This study	Ref 5	Ref 7	Ref 8
510 w	511 m	514 vw			
	488 m, vb				
477 s		470 m, p (0.24)	473 w, sh		
		} p (0.40)			
465 w, sh	467 m	459 m, p? (0.56)	465 m		466 m
451 w[b]	450 w[b]	433[b] vw	440 vw, ?	437 vvw, ?	
404 m	404 s				
388 vw		389 s, p (0.12)	394 m, p	388 vvw, ?	397 m
370 w, sh	365 s	361 vw	363 w		
332 w		331 w, p (0.54)			
		} p (0.61)	327 m		331 m
324 m	326 vvw	323 w, dp (0.73)			
212 w	210 w				
174 m	180 s				
160 m, sh	161 s	150 s, vb, dp (0.74)	156 s, vb	150 s, vb	
131 vw	130 s, br		127 s		
	115		106 s		

[a] Notation as in Table I. [b] Assigned as H_2O band.

Table III. Vibrational Spectra of $K_4W(CN)_8 \cdot 2H_2O$ in the CN Stretching Region[a]

Crystalline		Aqueous-solution Raman		
Raman (this study)	Infrared (ref 7)	This study	Ref 7	Ref 8
2138 s	2138 w	2135 vs, p (0.0)	2135 vs, p	2134 s
2129 m	2130 vs			
	2127 ?, vw, sh			
2125 ms	2125 vs			
		2118 ms		
2114 vs	2112 ?, vvw	} p (0.58)	2115 s, dp ?	2115 ms, b
		2104 w		
2100 vs	2101 m, sh			
2095 mw, sh	2096 v, vs			

[a] Notation as in Table I.

Table IV. Vibrational Spectra of $K_4W(CN)_8 \cdot 2H_2O$ in the Region 550–100 cm^{-1} [a]

Crystalline		Aqueous-solution Raman		
Raman (this study)	Infrared (ref 7)	This study	Ref 7	Ref 8
				619 m
				542 w
493 ms	488 s	484		
		} m, p (0.34)	482 ?, vw	486 m
466 mw	469 sh	471		
450 vw		442 w		
405 s	408 sh	404 s, p (0.24)	412 ?, vw	391 w
	391 s			
383 m	378 sh	372 w		
360 m	350 m, vb			
335 m		335 w,p (0.62)	338 ?, vw	339 m
	211 w, sh			
	179 w, sh			
	158 s	150 s, b, dp (0.73)	150 s, vb	156 s, vvb
	130			
	124 vw, b			
	108 w			

[a] Notation as in Table I.

ation $[I_{\parallel}(\text{obsd}_{\perp})]$, while the lower portion shows the component $I_{\perp}(\text{obsd}_{\perp})$. In both figures, curve resolution employing a Du Pont Model 310 curve analyzer is used to aid in precise frequency placement and in accurate measurement of depolarization ratios. It should be emphasized that *the structural conclusions drawn from our study are not contingent on curve resolution,* and, as will be discussed more fully below, this analysis is employed only in refining our vibrational arguments.

Discussion

Until recently, it appeared that the strongest evidence bearing on the solution structures of the octacyano complexes of Mo(IV) and W(IV) was that derived from

Table V. Predictions of $M(CN)_8^{4-}$ Fundamentals Allowed for Structures of D_{4d} and D_{2d} Symmetry

Point group	Number of allowed fundamentals and their symmetries D_{4d}	D_{2d}
(a) CN stretches		
Raman active	3 (A_1, E_2, E_3)	6 ($2A_1$, $2B_2$, 2E)
Infrared active	2 (B_2, E_1)	4 ($2B_2$, 2E)
Polarized Raman active	1 (A_1)	2 ($2A_1$)
Raman–infrared coincidences	0	4 ($2B_2$, 2E)
(b) Metal–carbon stretches and metal–carbon–nitrogen bends		
Raman active	8 ($2A_1$, $3E_2$, $3E_3$)	16 ($4A_1$, $2B_1$, $4B_2$, 6E)
Infrared active	5 ($2B_2$, $3E_1$)	10 ($4B_2$, 6E)
Polarized Raman active	2 ($2A_1$)	4 ($4A_1$)
Raman–infrared coincidences	0	10 ($4B_2$, 6E)

the electron paramagnetic resonance spectra of the presumably similar Mo(V) and W(V) complexes,[6b] where the anisotropy in the spin Hamiltonian parameters seemed best explained in terms of a square-antiprismatic conformation. Rationalization of this geometry in terms of specific solvation effects[3] implies that a D_{4d} symmetry would also be anticipated for $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ in a solution phase. However, an X-ray crystallographic investigation by Corden, Cunningham, and Eisenberg[13] shows that the anionic symmetry in crystalline $[(n\text{-}C_4H_9)_4N]_3[Mo(CN)_8]$ is distorted dodecahedral (D_2), and they conclude that the electron paramagnetic resonance *isotropic g* value is independent of environment, indicating retention of this structure in solution.[14] Although this does not necessarily indicate structural similarity for the octacyano complexes of Mo(IV) and W(IV), it seems possible that they could likewise exist in dodecahedral conformations in aqueous solution, and our laser–Raman data are consistent with this suggestion.

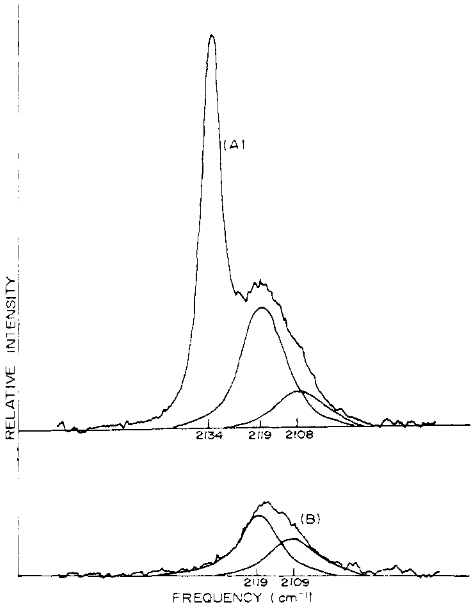

Figure 2. A laser-Raman polarization study of the CN stretching region (*ca.* 2100 cm^{-1}) of $Mo(CN)_8^{4-}$(aq): (A) $I_{\|}(\text{obsd}_{\perp})$, (B) $I_{\perp}(\text{obsd}_{\perp})$; slits, 2.5 cm^{-1}; scan rate, 10 cm^{-1} min^{-1}; time constant, 1 sec.

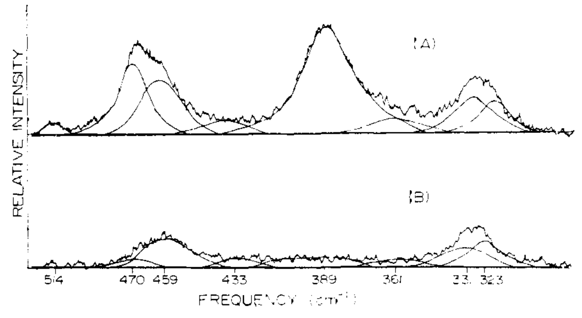

Figure 3. A laser-Raman polarization study of the low-frequency vibrations of $Mo(CN)_8^{4-}$(aq): (A) $I_{\|}(\text{obsd}_{\perp})$, (B) $I_{\perp}(\text{obsd}_{\perp})$; slits, 5 cm^{-1}; scan rate, 10 cm^{-1} min^{-1}; time constant, 1 sec.

For the octacyanide ions, the vibrational spectra are expected to consist of three distinct regions: (a) a CN stretching region (*ca.* 2100 cm^{-1}), (b) a region containing metal–carbon stretches and metal–carbon–nitrogen bends (550–300 cm^{-1}), and (c) a region of carbon–metal–carbon bending modes (below 250 cm^{-1}). The aqueous solutions of $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ exhibit only a single broad, depolarized band in the latter region at approximately 150 cm^{-1}, and the frequency range (250–0 cm^{-1}) will not be discussed further. A comparison of the number of allowed fundamentals under the point group symmetries D_{4d} (square antiprism) and D_{2d} (dodecahedron) is given in Table V for regions (a) and (b).

The spectra of the crystalline materials are clearly in better agreement with the predictions based on the known D_{2d} point symmetry[1-3] than those for a D_{4d} geometry. For example, although in region (b) of the $K_4Mo(CN)_8\cdot 2H_2O$ spectrum (550–300 cm^{-1}, Table II) only eight Raman-active modes are recorded, both the number of infrared absorptions (7) and the number of Raman–infrared coincidences (5) exceed those predicted for a square-antiprismatic structure. The CN stretching region (Table I) approximately corresponds

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(13) B. J. Corden, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, **9**, 356 (1970). We thank Professor Eisenberg for providing a copy of this manuscript prior to publication.

(14) The laser-Raman spectra of crystalline $[(n\text{-}C_4H_9)_4N]_3Mo(CN)_8$ and $[Co(NH_3)_6]Mo(CN)_8$ and of aqueous and CH_3CN solutions of $Mo(CN)_8{}^{3-}$ are discussed in a recent communication: T. V. Long, G. A. Vernon, and T. M. Loehr, submitted for publication.

to the predictions based on D_{2d} symmetry, but in this region, in contrast to regions (b) and (c), site-group effects are important. The $Mo(CN)_8^{4-}$ is located on a C_s special position,[1-3] and it is not unexpected that the CN stretching motions would be those most affected by site perturbations. Under C_s site symmetry, eight cyanide stretching fundamentals would be allowed, and all would be both Raman and infrared active. As shown in Table I, the resolution of the small but reproducible splitting in the 2129–2128-cm^{-1} Raman shift (an E mode under D_{2d} symmetry)[7] increases the number of observed Raman lines to seven, one more than allowed by D_{2d} selection rules, and every band is coincident with an infrared absorption. An examination of Tables III and IV shows that crystalline $K_4W(CN)_8 \cdot 2H_2O$ exhibits vibrational behavior similar to that of the molybdenum congener. Fundamental activity in the CN region obeys C_s site selection rules, but on the basis of the number of infrared peaks and the number of infrared–Raman coincidences, D_{2d} selection rules are more appropriate in region (b) (although only half the number of Raman-active shifts are recorded in this region).

We emphasize this dual dependence of spectral behavior on both site-group and point-group potential fields because we believe that it is cogent in understanding the modifications that occur in the Raman spectrum on dissolution. From Table V, it is seen that significantly simpler spectra are anticipated in both regions (a) and (b) for a square-antiprismatic structure, in which all cyanide ligands are equivalent, than for a dodecahedral arrangement, in which there are two nonequivalent sets of four ligands. Qualitatively, the changes in the Raman spectra of the CN region consequent to dissolution are those that might be anticipated for $D_{2d} \rightarrow D_{4d}$ structural interconversion: seven fundamentals that are strong in the spectra of the solids either disappear or coalesce into what we believe are three bands in the solution-phase spectra. For $Mo(CN)_8^{4-}$ the existence of three CN stretching Raman shifts can be verified (Figure 2) by noting the asymmetry in the depolarized spectrum and the frequency placement of its two components at 2119 cm^{-1} and 2109 cm^{-1}, clearly distinguished from the 2134-cm^{-1} band that is completely polarized ($\rho \simeq 0$). It was also found that it is impossible to fit the envelope of the upper spectrum in Figure 2 using only two-component bands of Gaussian, Lorentzian, or Gaussian–Lorentzian shape, but that a fit can be achieved with three components (at 2134, 2119 ± 2, and 2109 ± 2 cm^{-1}). Although Stammreich and Sala[5] resolved these same three peaks in their photographic study, only two bands (at *ca.* 2136 cm^{-1} and *ca.* 2120 cm^{-1}) were reported in previous laser–Raman investigations.[7,8] In both the latter publications, the coalescence–disappearance phenomenon in region (a) was taken as one ramification of structural conversion to a D_{4d} aqueous solution structure. However, careful measurement of the depolarization ratios of the 2134-cm^{-1} peak and the *complete residual band envelope* shows that there are at least two polarized bands in the CN stretching region ($\rho_{2134} \simeq 0$; $\rho_{\text{residual envelope}} = 0.54$), one more than would be allowed for D_{4d} symmetry, but congruent with the existence of the two A_1 modes anticipated for a dodecahedral structure. Curve resolution into three components illustrates this more clearly, and the band at 2119 cm^{-1} is polarized ($\rho_{2119} = 0.47$) while the band at 2109 cm^{-1} is depolarized ($\rho_{2109} = 0.71$). Furthermore, the 2109-cm^{-1} Raman shift is apparently coincident with the sole absorption measured in the infrared spectrum of the solution at 2110 cm^{-1}, a coincidence that would be allowed under D_{2d} symmetry. The polarization studies in the CN stretching region thus furnish positive evidence that the *$Mo(CN)_8^{4-}$ polyhedron is dodecahedral in crystalline and solution phases, and structural retention is affirmed.* The disparity between the numbers of fundamentals observed in the solution and solid-state spectra for an ion that retains the same point symmetry may be rationalized if one of the effects of C_s site symmetry on the solid-state spectrum is the intensification of Raman and infrared modes that would be active but weak under strict D_{2d} symmetry, in addition to the selection-rule-determined spectral modifications. The seeming disappearance of active vibrations upon dissolution can then be attributed to a relief of site potential perturbations. Of course, solvent broadening may prevent resolution of some bands in the solution-state spectra.

Complementary evidence for a dodecahedral conformation of $Mo(CN)_8^{4-}$ in solution can be gleaned from the frequency region of the Mo–C stretches and the Mo–C–N bends (Table II). Hartman and Miller[7] observed only two Raman-active modes in region (b) of their aqueous-solution spectrum, one of these likely a solvent mode, while Parish, *et al.*,[8] report the three-band maxima at 466, 397, and 331 cm^{-1}. The top spectrum in Figure 3 clearly contains at least six bands in this region (at 514, 470, 459, 389, 360, and *ca.* 330 cm^{-1}), even if one does not take advantage of curve fitting procedures. Analysis of the total band contour shows an additional shift at 433 cm^{-1}, attributed to a water libration, and a resolution of the *ca.* 330-cm^{-1} band into two peaks at 331 cm^{-1} and 323 cm^{-1}. With the exception of our graphical resolution of the 330-cm^{-1} band and the observation of the weak but definite shift at 514 cm^{-1}, there is gratifying agreement between our spectrum and that of Stammreich and Sala.[5] Although the simplicity of this region of the spectrum has again been taken to imply structural conversion,[8] one sees that, except for the band at 404 cm^{-1} that is not observed in the solution-state spectrum and perhaps masked by the intense shift at 389 cm^{-1}, *every Raman mode that is measured in the crystalline material in this region is also measured for aqueous $Mo(CN)_8^{4-}$.* This one-to-one correspondence between the crystalline and aqueous-phase spectra in region (b), where site-group effects on the solid-state spectra are not apparent (*vide supra*), is persuasive evidence that the octacyanomolybdate(IV) polyhedron is identical in both phases.

Substantiation of the postulated structural retention is found in the polarization ratios measured for the Raman shifts in region (b). Visual examination of Figure 3 plainly shows that the bands at 470 cm^{-1} and 389 cm^{-1} are nearly totally polarized, and the total band envelope centered at *ca.* 330 cm^{-1} may likewise be shown to be polarized ($\rho_{330} = 0.61$). Therefore, there are at least three polarized Raman lines in this region, and this is one in excess of the two A_1 modes allowed by D_{4d} selection rules, but one less than the four A_1 modes permitted for a dodecahedral structure. If one employs curve resolution of the *ca.* 330-cm^{-1} envelope into components at 331 cm^{-1} and 323 cm^{-1}, it appears that it is the higher frequency component that is polarized. Moreover, comparing the solution-phase Raman spectrum (which is isomorphic with the spectrum of the crystalline material) with the infrared of the solid, we see that every Raman mode except for the polarized A_1 modes coincides with an absorption. This would be expected for a D_{2d} conformation, but a square-antiprismatic structure would require all four coincidences to be accidental.

For the tungsten(IV) compound, arguments directly analogous to those presented above may be framed. Succinctly stated, in the CN stretching region of the solution-phase spectrum there are two polarized bands (2135 cm^{-1} and 2118 cm^{-1}) and in the 550–300-cm^{-1} region there are three polarized bands at (484, 471 cm^{-1}), 404 cm^{-1}, and 335 cm^{-1}, inconsistent with the number predicted for D_{4d} symmetry, but commensurate with the number allowed under D_{2d} selection rules. The 2104-cm^{-1} Raman shift of the aqueous material appears to be coincident with the infrared absorption measured at 2105 cm^{-1},[7] and coincidences are also found in region (b). Also, every W–(CN) stretch or W–C–N bend that is resolved in the spectrum of the solid material is present in the aqueous-solution spectrum. Therefore, it is unlikely that a change from a D_{2d} to a D_{4d} conformation occurs upon dissolution of $K_4W(CN)_8 \cdot 2H_2O$.

In summary, in contradiction to the suggestions from earlier vibrational investigations,[5,7,8] we conclude that the dodecahedral structures known for octacyanomolybdate(IV) and octacyanotungstate(IV)[1–3] in crystalline environments are maintained in aqueous solution. This interpretation is based on three lines of vibrational evidence: (a) the number of polarized Raman shifts in the metal–cyanide stretching region and in the M–CN stretching, M–C–N bending region of the aqueous-solution spectrum exceeds that allowed for D_{4d} symmetry; (b) in the 550–300-cm^{-1} region, where site-group effects are not observed, every Raman line of the solid is also recorded in the spectrum of the solution; and (c) the number of infrared–Raman coincidences (none of which should occur under D_{4d} point symmetry) is too large for all to be dismissed as of accidental origin. Unless specific solvation effects are operative, one may infer that the D_{2d} polyhedron is more stable than a D_{4d} structure and that the isolated ions would also exhibit a dodecahedral ligand disposition.