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Transition Metal Eight-Coordination. VI. Isomerization through Electronic and Environmental Effects—Electron Spin Resonance, Magnetic Circular Dichroism, and Electronic Spectra of Octacyanotungstate(IV) and -(V)[1]

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The octacyanotungstate(IV) ion retains a dodecahedral geometry in aqueous solution, with the first spin-allowed d–d transition established as $^1E \leftarrow {}^1A_1$ from magnetic circular dichroism spectroscopy. The other spin-allowed d–d transitions appear to be nondegenerate and are logically transitions to the $^1B_1$ and $^1A_2$ excited states. Both dodecahedral and antiprismatic ground states are evident for the octacyanotungstate(V) ion from electron spin resonance measurements, which indicate that the ground-state stereochemistry is both cation and solvent dependent.

Introduction

The octacyanometalate ions of molybdenum and tungsten are inert to substitution,[2] exist in two polytopal geometries[3] in the solid state,[4] appear to be nonrigid in solution,[5] and exist in two oxidation states.[6] These properties make the octacyano ions ideal for evaluating the stereochemical effects of d-electron interactions (particularly d^1 *vs.* d^2), counterions, and solvents in eight-coordinate systems. Using a variety of techniques, a multitude of investigators have studied the structures of these d^1-d^2 systems in the solid state and in solution, often arriving at seemingly conflicting results, particularly in solution.

The X-ray studies of $K_4[Mo(CN)_8]\cdot 2H_2O$ have shown that the octacyanomolybdate(IV) anion in this salt exists in a dodecahedral configuration for which C_s site symmetry is imposed by the lattice.[4a,b] However, another study has shown that the $H_4[W(CN)_8]\cdot 6H_2O$ solid assumes an approximate square-antiprismatic structure.[4c] Infrared and Raman studies[7] have been in general disagreement over the structure of the octacyano ions, although the most definitive study using polarized Raman spectra[7a] has shown that the $K_4[Mo(CN)_8]\cdot 2H_2O$ and $K_4[W(CN)_8]\cdot 2H_2O$ complexes are both C_s in the solid state and appear to remain dodecahedral upon dissolution. Ultraviolet and visible absorption spectra of these complexes in aqueous solution have been given both dodecahedral and antiprismatic interpretations.[8] Furthermore, carbon-13 nuclear magnetic resonance spectroscopy studies[5a,d,e] have been equally inconclusive. The possibility of a rapid equilibrium between the dodecahedral and antiprismatic states has been suggested, but antiprismatic geometry or accidental signal degeneracy is an alternate possibility.

The d^1 species have been fraught with similar uncertainties. X-Ray structures are known for both geometries;[4e,f] and electronic,[8,9] vibrational,[7] and electron spin resonance[4e,10] spectral results have been given dual interpretations. For example, whereas the electron spin resonance spectra of $K_3[Mo(CN)_8]\cdot 2H_2O$ and $K_3[W(CN)_8]\cdot 2H_2O$ glasses or solid solutions exhibit a pattern anticipated for an antiprismatic arrangement with a $^2A_1$ ground state,[10] the interpretation of the spectra has been questioned by Cordon, Cunningham, and Eisenberg.[4a] They found an isotropic $\langle g \rangle$ value for the solid tetra-*n*-butylammonium salt identical with that reported for the potassium salt,[10] whereas the onium salt possesses a slightly distorted dodecahedral structure of D_2 symmetry in the solid state.[4a]

Electron spin resonance, electronic absorption, electronic reflectance, and magnetic circular dichroism spectra from our laboratory confirm the stereochemical mobility of the octacyanotungstate(V) ion and demonstrate a definitive

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(1) (a) Taken in part from the Ph.D. dissertation of R. A. Pribush, University of Massachusetts, 1972. (b) Presented in part at the 165th National Meeting of the American Chemical Society, Dallas, Tex., 1973; see Abstracts, No. INOR 105. (c) Part V: R. D. Archer and D. A. Drum, *J. Inorg. Nucl. Chem.*, in press. (d) Part IV: R. D. Archer, W. D. Bonds, Jr., and R. A. Pribush, *Inorg. Chem.*, 11, 1550 (1972).

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Table I. Summary of $[W(CN)_8]^{3-}$ Electron Spin Resonance Spectra

Cation	Phys state	Temp, °C	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle^a$	$A_{\parallel}$	$A_{\perp}$	$\langle A \rangle^a$	Comments[b]
Na	Powder	−196	1.986	1.963	1.971				Figure 1
Na	H_2O	25			1.970			56	Symmetric
Na	H_2O	−196			1.973				Symmetric
Na	H_2O–glyc	−196	1.986	1.964	1.971	27	69	55	
K	H_2O–glyc	−196	1.982	1.968	1.972	(19)	68.5	(52)	Ref 10a
Na	CH_3OH	25			1.969			56	Symmetric
Na	CH_3OH	−196	1.986	1.964	1.971	28	67	54	
Na	CH_3CN	−196			1.973				Symmetric[c]
K	Powder	−196			1.972				$g_{\parallel} > g_{\perp}$; Figure 1
K	CH_3OH	25			1.969			56	Symmetric
K	CH_3OH	−196	1.986	1.964	1.971	27	67	54	
K	CH_3OH	−196	1.989	1.966	1.974	26	66	53	Ref 10b
K	CH_3COOH	25			1.970			54	Symmetric
K	CH_3COOH	−196	1.986	1.964	1.971	28	66	54	
$(n\text{-Bu})_4N$	Powder	25			1.970				Symmetric
$(n\text{-Bu})_4N$	Powder	−196			1.973				Symmetric
$(n\text{-Bu})_4N$	Powder	−269			1.973				Symmetric; Figure 1
$(n\text{-Bu})_4N$	1% powder[d]	−196			1.970				Symmetric
$(n\text{-Bu})_4N$	CH_3CN	25			1.969				Symmetric
$(n\text{-Bu})_4N$	CH_3CN	−196			1.971				$g_{\parallel} > g_{\perp}$
$(n\text{-Bu})_4N$	CH_3COOH	−196			1.971				$g_{\parallel} > g_{\perp}$
$(n\text{-Bu})_4N$	CH_3COOH	−269			1.973				$g_{\parallel} > g_{\perp}$
$(n\text{-Bu})_4N$	$n\text{-}C_4H_9OH$	−196	1.984	1.963	1.970	28	66	53	
$(n\text{-Bu})_4N$	$n\text{-}C_4H_9OH$	−269	1.985	1.964	1.971	28	67	54	
Ag	Powder	−196			1.977[e]				Very broad[e]

[a] Calculated where $g_{\parallel}$ and $g_{\perp}$ separable; otherwise the observed $\langle g \rangle$ or psuedo $\langle g \rangle$; $\langle A \rangle$ is analogous. [b] $g_{\parallel} > g_{\perp}$ refers to asymmetric signals for which difinitive breakdowns are not possible. [c] Possibly $g_{\parallel} > g_{\perp}$. [d] Tetra-*n*-butylammonium bromide matrix. [e] Symmetric but very broad; half-width >150 G.

electronic spectral state ordering for the three spin-allowed d-d electronic transitions of the $[W(CN)_8]^{4-}$ ion in aqueous solution.

Results

The electron spin resonance results for the octacyanotungstate(V) species are tabulated in Table I. Representative spectra showing the cation and solvent effects are shown in Figures 1 and 2. The dramatic spectral differences found in going from sodium as a cation to potassium and tetra-*n*-butylammonium (onium) ions as solid powders (Figure 1) are also evident in the solvent dependence of solid solution electron spin resonance spectra of the sodium salt at liquid nitrogen temperature (Figure 2). Whereas solid water and acetonitrile solutions of sodium octacyanotungstate(V) have a symmetrical electron spin resonance signal, anisotropic parameters can be obtained from methanol and aqueous glycerol solid solutions under comparable conditions. Furthermore, whereas the onium salt solutions possess a slightly asymmetrical signal in acetonitrile and in acetic acid at low temperatures, only the 1-butanol spectrum can be definitively resolved into anisotropic parameters. Even though the spectrum of the onium salt in acetic acid is asymmetric at liquid helium temperature, $g_{\parallel}$ is only a slight bluge in the signal. On the other hand, the potassium salt in acetic acid exhibits cleanly separated $g_{\parallel}$ and $g_{\perp}$ signals, even at liquid nitrogen temperature. A tetra-*n*-butylammonium bromide matrix of the onium complex exhibits an electron spin resonance spectrum which is identical with that of the onium salt powder.

The visible absorption spectra of the octacyanotungstate(V) ion in various environments are listed in Table II. The onium powder appears colorless to the eye, whereas the sodium salt appears yellow to deep orange, depending on crystallite size and temperature. The color intensity is much lower at liquid nitrogen temperature than at room temperature as anticipated for a vibronically coupled transition.

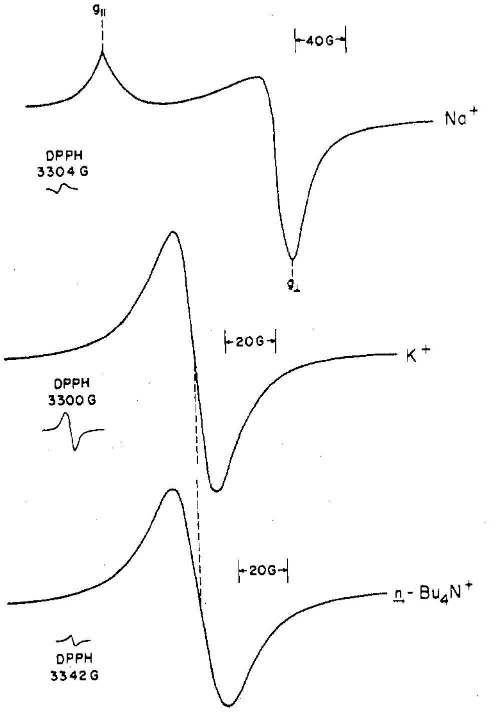

Figure 1. Solid powder electron spin resonance spectra of the $M_3[W(CN)_8]$ type, where M = Na, K, or $(n\text{-Bu})_4N$.

Interestingly, flat, light yellow needles of the sodium salt crystallize from hot acetonitrile. These needles are different from the orange columnar crystals obtained from aqueous solution. The needles are very hygroscopic, producing an orange solution (with the 22-kK absorption peak), and were not investigated further.

Magnetic circular dichroism spectra with the potassium salts of W(IV) and Mo(IV) and the sodium salt of W(V) in aqueous solutions and a comparable spectrum of the onium salt in acetonitrile were obtained in order to understand further the electronic properties of these complexes in relationship to their structures. See Table III and Figure 3.

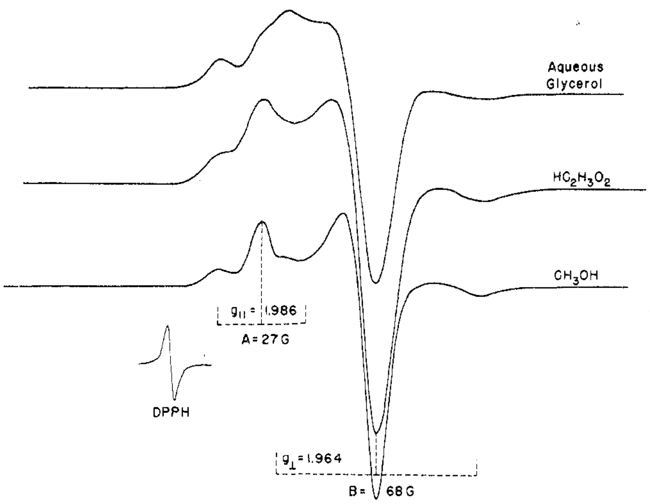

Figure 2. Electron spin resonance of the $[W(CN)_8]^{3-}$ ion in solid-solution (glass) matrices: sodium salt in aqueous glycerol, potassium salt in acetic acid, and sodium salt in methanol. The sodium salt in acetonitrile looks like the tetra-*n*-butylammonium salt shown in Figure 1.

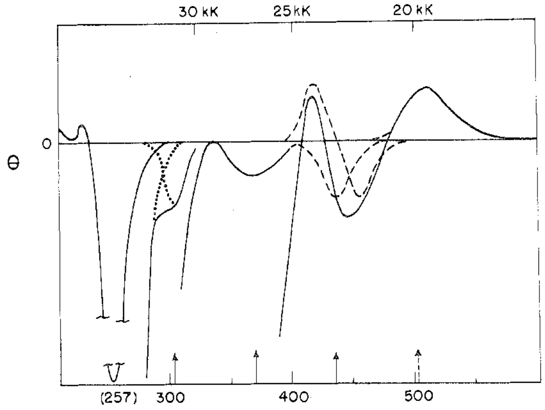

Figure 3. Magnetic circular dichroism spectrum of aqueous $[W(CN)_8]^{4-}$ (potassium salt) together with a gaussian breakdown of the 435-nm d–d transition into MCD *A* and *B* terms. The energies of the three spin-allowed d–d transitions are shown as solid arrows and the band near 500 nm (broken arrow) corresponds to a spin-forbidden transition in the absorption spectrum of the complex ion.

Table II. Visible Electronic Transitions in $[W(CN)_8]^{3-}$ Species

Environment	$\bar{\nu}$(max), kK	Environment	$\bar{\nu}$(max), kK
Aqueous (Na^+)	23.0[a]	Mull, Ag^+ salt	19.1
Mull, Na^+ salt	22.0[b]	Aqueous $NH_3(Ag^+)$	22.8-23.8
Mull, K^+ salt	22.8	Acetonitrile (onium)	None
Mull, onium salt	None	Acetonitrile (Na^+)	None[c]

[a] $\epsilon = 1.3$ when corrected for charge-transfer overlap; the peak remains in the presence of strong oxidizing agents, specifically H_2O_2, cerium(IV), and permanganate; but ϵ appears concentration dependent even over the narrow range of concentrations through which it can be observed. [b] Both at +25 and −195°; sharper and weaker at −195°. [c] Even $Na_3[W(CN)_8]$ crystals from acetonitrile are only light yellow.

Table III. Absorption and MCD Spectral Comparisons for Octacyano Complexes[a]

$Na_3[W(CN)_8]$(aq)		$[(n\text{-}Bu)_4N]_3[W(CN)_8]$(in CH_2Cl_2)	
Uv–visible	MCD	Uv–visible	MCD
23.0 sh	23.7 max		
28.0	27.6 max	27.9	27.6 max
29.6	29.4 sh	29.5	29.5 sh
32.8 sh	32.4 infl	32.8	32.8 sh
		37.0	
39.2 sh	38.8 infl	38.9	38.9 infl
41.2	41.5 infl	41.3	41.3 infl
44.1 sh	44.1 infl	43.7	43.7 min
$K_4W(CN)_8$(aq)		**$K_4Mo(CN)_8$(aq)**	
Uv–visible	MCD	Uv–visible	MCD
19.9 sh[b,c]	19.6 max	19.6[b] sh	19.0 max
23.0 sh	23.3 infl[d]	23.3 sh	23–24 br sh
27.0	27.0 min	27.3	27.5 min
33.0 sh[b]	32.7 min	35.7	35.8 min
36.6 sh[b]		37.5[b] sh	
40.0	39.7 min	41.4	41.3 min
43.7 sh	43.5 max		

[a] Absorption peak and MCD terms in kK. Key: sh, shoulder; max, maximum; infl, inflection point; min, minimum; br sh, broad shoulder. [b] See ref 8b for gaussian analysis of absorption spectra. [c] Reference 8b suggests spin-forbidden transition here. [d] Gaussian analysis gives MCD *A* and *B* terms at 23.0 kK; see Figure 3.

Discussion

Electron Spin Resonance Spectra. For an axially symmetric complex containing a single unpaired electron, two electron spin resonance (esr) signals are expected for the basic spectrum, on which satellite hyperfine peaks are superimposed due to a 14% isotopic abundance of tungsten-183 ($I = {}^1/_2$). Using first- and second-order perturbation theory McGarvey[10a] derived equations for the spin-Hamiltonian parameters of the two energetically favorable geometries which the $[M(CN)_8]^{3-}$ ion can assume. For the dodecahedron the equations take the form

$$g_{\parallel} = 2.0023 - \frac{8\lambda}{E(d_{xy}) - E(d_{x^2-y^2})}$$

$$g_{\perp} = 2.0023 - \frac{2\lambda}{E(d_{xz}, d_{yz}) - E(d_{x^2-y^2})}$$

for a ${}^2B_1$ ground state. For reasonable values for the spin-orbit coupling parameter and the energy separations, one predicts that $g_{\perp} > g_{\parallel}$. Likewise, for the hyperfine splitting constants one predicts that $|A_{\parallel}| > |B_{\perp}|$.[10a]

The square antiprism has corresponding equations

$$g_{\parallel} = 2.0023$$

$$g_{\perp} = 2.0023 - \frac{6\lambda}{E(d_{xz}, d_{yz}) - E(d_{z^2})}$$

having magnitudes $g_{\parallel} > g_{\perp}$ and similarly $|B_{\perp}| > |A_{\parallel}|$ for a ${}^2A_1$ ground state.[10a]

The derivative esr spectra of $K_3[Mo(CN)_8]$ and $K_3[W(CN)_8]$ reported in the literature[10] clearly exhibit the features predicted for a square antiprism; however, the magnitudes of the spin-Hamilitonian parameters obtained from the spectra are not in accordance with a simple crystal field approach. For instance, $g_{\parallel}$ is less than 2.0023. Obvious explanations for this discrepancy include the following. (1) The spin-orbit coupling factor is too large for the second-order perturbation theory approximation. The fact that the deviation from 2.0023 is less for the molybdenum complex than for the tungsten analog reflects the decreasing importance of spin-orbit coupling as one ascends a family. (2) Cyanide complexes are significantly covalent in nature, disallowing the use of pure d orbitals. (3) The geometry of the octacyanide anion deviates from the idealized D_{2d} dodecahedral or D_{4d} square-antiprismatic point group.[4]

McGarvey[10a] was unable to account for the first two effects by using an orbital reduction factor. Nevertheless, on the basis that $g_{\parallel} > g_{\perp}$ and $|B_{\perp}| > |A_{\parallel}|$ for $K_3[Mo(CN)_8]$

and $K_3[W(CN)_8]$ in glycerol and methanol glasses, these complexes were assigned a square-antiprismatic structure in solution. The same salts doped into a C_s-distorted D_{2d} matrix [the corresponding molybdenum(IV) and tungsten(IV) salts] exhibit $g_\perp > g_\parallel$ as predicted for dodecahedral symmetry with a $^2B_1$ ground state.[10a]

Corden, Cunningham, and Eisenberg[4e] obtained a single-line esr spectrum for $[(n\text{-Bu})_4N]_3[Mo(CN)_8]$ both with the polycrystalline sample and in solid acetonitrile solution. The isotropic $\langle g \rangle$ value is 1.991 ± 0.001, which is invariant for the two states at −196° and for the polycrystalline sample at room temperature. Within experimental error this value is in agreement with the $\langle g \rangle$ values obtained for the K^+ salt in water and glycerol.[10] The onium salt was shown by their (Corden, *et al.*[4e]) single-crystal X-ray structural determination to be a distorted dodecahedron (D_2) and they suggested that the equivalent $\langle g \rangle$ value is consistent with equivalent structures for both the onium and the potassium salts. A ground-state orbital having both d_{z^2} and $d_{x^2-y^2}$ character was used to explain the ordering of the anisotropic $\langle g \rangle$ values in the potassium salt in glycerol and methanol. An implicit suggestion is put forth that on this basis esr is not a sensitive tool for determining the stereochemistry of eight-coordinate complexes.

The information derived from the electron spin resonance spectra reported herein indicates that the analysis of the esr data by Corden, *et al.*,[4e] is partially untenable. The X-ray study of $Na_3[W(CN)_8]\cdot 4H_2O$[4f] showed that the structure of the anion is approximately square antiprismatic. The esr spectrum of a polycrystalline sample of the sodium salt reported here is identical with the solid methanol, glycerol, and acetic acid solution spectra, *sans* hyperfine structure, of the sodium and potassium salts, indicating (1) that there is no change in the gross structure of the W(V) salt in these solid solutions and (2) that the sodium and potassium salts in frozen methanol, glycerol, and acetic acid solutions have square-antiprismatic structures indistinguishable *via* electron spin resonance. Hence it appears that the treatment of the potassium salt by McGarvey[10a] is essentially correct. The deviations of the spin-Hamiltonium parameter from theoretical values are most likely due to the net effects of spin-orbit coupling, covalency, and distortions from D_{4d}, none of which is included in the simple crystal field treatment.

The near equivalence of isotropic $\langle g \rangle$ values for all salts is fortuitous and cannot be used to characterize either isomer. Distortions from idealized octacoordinate geometries and/or stereochemical nonrigidity are sufficient to cause $\langle g \rangle$ values to coalesce to 1.971 for the tungsten complexes and 1.992 for the molybdenum complexes, regardless of the ground-state geometries.

The real problem concerns the interpretation of the single-line spectra for the salts in various environments. Solution of this enigma lies in the interpretation of the single, completely symmetric esr signal for the polycrystalline $[(n\text{-Bu})_4N]_3[W(CN)_8]$, which is presumably isomorphous to its molybdenum analog, known to have D_2 symmetry and a symmetric esr signal.[4e] Using the least-squares trapezoidal planes criterion of Lippard and Russ,[11] the deviation of the anion from idealized dodecahedral geometry is only 2.3°. One might, therefore, anticipate a $g_\perp > g_\parallel$ esr pattern, the reverse of which is found for the square-antiprismatic sodium salt. Although the spectrum is considerably broader than that of the polycrystalline sodium salt, an asymmetric signal is expected for a dodecahedral complex with $g_\perp \neq g_\parallel$, for the $g_\perp$ signal should have a greater intensity than the $g_\parallel$ signal. The acetonitrile glass spectrum consists of a solitary signal, which is overall broader than the polycrystalline signal; however, the acetonitrile glass spectrum is clearly asymmetric. The signal appears to be a broadened $g_\parallel > g_\perp$ spectrum. Further evidence is the existence of a broad flat region in the vicinity of the high-field $B_\perp$ hyperfine peak found in the sodium and potassium salt spectra. The differences in the spectra seem to indicate that the solid and solution geometries of the tetra-*n*-butylammonium salt are not the same and that in the acetonitrile glass, $[(n\text{-Bu})_4N]_3[W(CN)_8]$ is "more square antiprismatic" than in the crystalline state.

The solid-state broadening in the tetra-*n*-butylammonium salt spectrum cannot result from intermolecular metal–metal interactions because the closest Mo–Mo distance is 11.39 Å. Delocalization through the cyano ligands may account for the broadened signal. The relative freedom of the $[M(CN)_8]^{3-}$ species within the lattice of this extremely loosely packed complex[4e] and the completely symmetric esr signal initially appeared indicative of a stereochemically nonrigid structure for the octacyanometalate(V) anion; however the signal is virtually identical at liquid helium temperature, where nonrigidity appears very improbable.

The possibility that the onium powder electron spin resonance spectral symmetry is a result of tungsten–tungsten interactions *via* the unsaturated cyano ligands is ruled out by the onium bromide salt matrix spectrum. The matrix spectrum is identical with the neat onium powder spectrum.

Corden, Cunningham, and Eisenberg[4e] have suggested that the single *g* value results from low symmetry. That is, in intermediate geometries between the D_{4d} and D_{2d} point groups pure d_{z^2} or $d_{x^2-y^2}$ ground states no longer occur. Instead, the mixing of states occurs to a sufficient extent that the $g_\parallel$ and $g_\perp$ signals become coincidentally superimposed, appearing as a unitary signal. The extent of the mixing depends on the distortion of the anion from the idealized geometries. The distortion is a function of the environment. By varying the environment the forces acting on the ion should change sufficiently for different eight-coordinate geometries to occur as ground states.[3]

The esr studies are consistent with this explanation. The powder spectra indicate that the nature of the cation and/or the solvation sphere of the cation has a significant influence on the geometry of the $[W(CN)_8]^{3-}$ anion. Hence the small sodium ion has a sufficient steric or electrostatic perturbing influence on the octacyanide to yield a square antiprism. In the crystal each sodium cation is surrounded by an octahedron of water molecules and cyanide nitrogen atoms, forming a highly structured network. The natural forces (without d-electron considerations) also favor the antiprism.[3]

In comparison, the lattice interactions in the tetra-*n*-butylammonium salt crystal are minimized by a disordered, large cation; the shielding effect of the bulky *n*-butyl groups appreciably limits counterion interaction. Therefore, the $[W(CN)_8]^{3-}$ anion in this salt, which has been shown to be D_2 dodecahedral, should closely approach an unperturbed, low energy state geometry. Apparently the loss of an electron from the D_{2d} $[W(CN)_8]^{4-}$ moiety reduces the d-electron perturbation sufficiently to allow a distortion away from the idealized dodecahedron. In the presence of strong counterion and solvent interactions the effect of the single remaining d electron becomes subservient to steric effects and a square antiprism occurs, as is being approached by the crystalline sodium salt.[4f]

The esr spectrum of the potassium salts shows that a cation larger than sodium can have an effect similar to the

(11) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 7, 1686 (1968).

onium groups. The slightly asymmetric signal indicates that the potassium ion, its related waters of hydration, and the natural steric preference for the antiprism distort the ion toward a square antiprism. The shorter, broader portion ($\sim g_{\parallel}$) of the signal is downfield from the taller, narrower ($\sim g_{\perp}$) signal.

For the silver salt large interaction of the Ag^+ ions with the nitrogens of the cyanide groups is anticipated. The broadness of the esr peak ($W_{1/2} = 152.5$ G) might be indicative of an intermolecular exchange process occurring due to such a contact. Also the "$\langle g \rangle$" value is 1.977 ± 0.001, closest of all the salts to the free electron value, indicating a greater delocalization of the electron than for the alkali and tetra-*n*-butylammonium salts. Unfortunately the peak's broadness obscures the spectrum's details.

The solvent effect on the structure of $[W(CN)_8]^{3-}$ is quite evident from the frozen-solution esr studies. The sodium salt does not change structure upon dissolution in methanol or aqueous glycerol; the esr spectra yield parameters identical with those of the powder spectrum. In acetonitrile, however, the effect of the sodium ion appears to be decreased by the solvent and a D_2 structure results as evidenced by the single symmetric signal.

The potassium salt, on the other hand, apparently changes its structure upon dissolution in methanol or acetic acid from a distorted D_2 to a D_{4d} geometry. Demonstrating that the solvent effect occurs simultaneously with the cation perturbation, dissolution of the tetra-*n*-butylammonium salt in acetic acid does not result in the D_{4d} esr spectrum noted for the potassium salt. Instead a D_2 signal occurs which is distorted toward a D_{4d} signal. Interestingly, the tetra-*n*-butylammonium salt, shown to be D_2 in the solid state appears "less dodecahedral" in acetonitrile than the Na^+ salt, which is D_{4d} in the crystalline form!

In 1-butanol the solvent effect overcomes the cation effect and the tetra-*n*-butylammonium salt yields a D_{4d} esr pattern similar to those of the sodium and potassium salts in methanol.

Although the water-glycerol spectrum for the sodium salt is similar to the spectrum reported by McGarvey[10a] for the potassium salt, calculated values for $g_{\parallel}$ and $g_{\perp}$ differ because of different methods of interpreting the spectra. Analyzing the center line by applying lorentzian and gaussian broadening functions to theoretical curves, McGarvey found little deviation in the position of the inflection point and, hence, chose that portion of the spectrum to abstract a value for $g_{\perp}$.[12] Using solvents of different polarity which yield spectra exhibiting various degrees of line broadening, however, we observed that the major peak of the center line also occurred at a consistent field. We therefore utilized this peak to calculate a $g_{\perp}$ value in accordance with the method of Sands.[13] For this reason our values are slightly lower than those of McGarvey.[10a]

The difference in $g_{\parallel}$ values results from what we feel is McGarvey's misinterpretation of a deceptive feature of the water-glycerol solution spectrum. As the dielectric constant of the solvent is increased from that of methanol (ϵ 32.6) to that of water (ϵ 78.5)-glycerol (ϵ 42.5)[14] considerable dipolar broadening occurs, which in the case of a pure aqueous sample obliterates the minor features of the spectrum. In spite of its low dielectric constant (ϵ 6.19) glacial acetic acid has an intermediate broadening effect, probably because of hydrogen bonding to the cyano ligands. The nature of this broadening effect enables the high-field $A_{\parallel}$ hyperfine peak to assume a greater apparent intensity than that of the actual $g_{\parallel}$ peak, which occurs as a shoulder in the water-glycerine spectrum. The relative intensity of the $g_{\parallel}$ peak is more accurately represented in the methanol spectrum. Misled by the abnormal intensity of the $A_{\parallel}$ hyperfine peak in the water-glycerine spectrum, McGarvey took this peak as his $g_{\parallel}$ signal, yielding a smaller $g_{\parallel}$ value than that of the true $g_{\parallel}$ signal which occurs at lower field.

Since Hayes[10b] did not present his methanol spectrum or his method of spectral analysis, the small deviation of his g values from those reported here may be the result of differences in instrument calibration. There is reasonable agreement of Hayes' hyperfine splitting constant with those reported in this paper; although Hayes suggested that each major peak has two satellite peaks, the low-field $B_{\perp}$ hyperfine peak was not evident in our methanol spectrum.

Electronic Spectra. The electronic absorption and reflectance spectra provide further evidence for the solvent and cation effects on the structure of $[W(CN)_8]^{3-}$. In fact, the energy of the first d-d transition appears to be diagnostic for $[W(CN)_8]^{3-}$ polytopes. Hexachlorobutadiene mull spectra of $Na_3[W(CN)_8]$, which is the only salt studied that gives a distinct square-antiprismatic esr spectrum for a powdered sample, contain a single strong peak at 22.0 kK. The energy of this transition is shifted from the nearest nonaqueous solution spectral transition by 6.0 kK and by 1.0 kK from the 23.0-kK peak observed for the $Na_3[W(CN)_8]$ salt in concentrated aqueous solution. The mull spectrum of $K_4[W(CN)_8]$ shows a weak peak at 22.8 kK,[1a] within experimental error of the analogous peak in aqueous solution, indicating that the 22.0-kK peak in the $Na_3[W(CN)_8]$ mull spectrum is not caused by $[W(CN)_8]^{4-}$ impurity. Furthermore, oxidizing agents do not affect the 23.0-kK peak either. Therefore, other tungsten(IV) impurities are likewise eliminated, although some nonoxidizable impurity cannot be absolutely eliminated as the cause of the 23-kK peak. The molar extinction coefficient of this peak has a low value (<2) and appears to be concentration dependent indicating the "antiprismatic character" being induced in the aqueous solutions is a result of ion pairing. The lack of observable "antiprismatic character" in the aqueous esr spectra (Table I) is a result of the minimal ion pairing at such low concentrations and/or the dipolar broadening which occurs in aqueous esr spectra. At these low concentrations, the 23.0-kK absorption peak is not observable either.

The mull spectrum of $[(n\text{-}Bu)_4N]_3[W(CN)_8]$ contains no peaks in the visible region, which indicates that the first transition observed in the other salts is blue-shifted under the 28.0 kK peak for the D_2 dodecahedral species. The $K_3[W(CN)_8]$ mull spectrum weak peak at 22.8 kK might be due to the presence of some $K_4[W(CN)_8]$ or a third polytope. The powder esr spectrum of the potassium salt had only a slight square-antiprismatic distortion of the solitary signal. If the 22.8-kK peak is a $K_3[W(CN)_8]$ d-d transition, the energy at which this transition occurs for the three salts is in the order tetra-*n*-butylammonium > potassium > sodium, and the powder esr spectrum of the potassium salt is intermediate to those of the other two (although more similar to the tetra-*n*-butylammonium salt spectrum). On this basis $K_3[W(CN)_8]$ should have a structure further distorted from D_{2d} than the tetra-*n*-butylammonium salt, but not quite D_{4d} square antiprismatic, based on both esr and electronic absorption spectral observations. Because the esr

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(12) B. R. McGarvey, personal communication.

(13) R. H. Sands, *Phys. Rev.*, 99, 1222 (1955).

(14) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1970, pp 99-101.

spectra of the potassium salt are only slightly distorted and the d–d peak appears weak, a mixture of a predominant D_2 isomer plus a small amount of another isomer having antiprismatic character is also possible.

The mull spectrum peak position (19.1 kK) of the silver salt might be indicative of a square-antiprismatic structure. The esr signal is too broad to be useful and perturbations on coordinated cyanide by the silver ion apparently lower the energy of the first d–d transition. In fact, the silver salt has definite shoulders at 22.8–23.8 kK in ammonium hydroxide solution. Saturated solutions of other salts in acetonitrile and acetic acid appear slightly yellow, perhaps indicating that the 23-kK peak exists under the tail of the more intense band at 28.0 kK.

Differences in the spectra are also observed in the uv region for the sodium salt compared to the tetra-*n*-butylammonium salt in acetonitrile solutions and compared to the silver salt in ammonium hydroxide. These bands are charge-transfer transitions and would be sensitive to solvent and/or cation effects.

Because the tetra-*n*-butylammonium salt has a poorly packed lattice, the D_2 structure of this salt is considered more typical of the structure which $[W(CN)_8]^{3-}$ should exhibit where external perturbations and ligand–ligand are lower than the d^1 perturbation. Apparently the single d-electron perturbation finds difficulty in maintaining the D_{2d} dodecahedron, which is the preferred polytope for d^2 $[W(CN)_8]^{4-}$ complexes[7a] and the polytope into which the d^1 ion can be forced by precipitation into the d^2 lattice.[10a] The d-electron interactions apparently favor the dodecahedron. Removal of half the perturbation, as in the d^1 complexes, results in other structure-orientating factors competing with the d-electron effect and the $[W(CN)_8]^{3-}$ anion distorts toward the antiprismatic structure under a wide variety of conditions. Extending the concept, the hypothetical d^0 complex $[W(CN)_8]^{2-}$ would be square antiprismatic. Calculations neglecting d-electron effects do favor the antiprism.[3]

Changes in the solution electronic spectra of these complexes, in which the d-electron effect favors the D_2 configuration, should be observed upon decreasing the temperature of the solutions from ambient to lower temperatures. In the extreme, when glasses are formed, the external perturbations of the solvent and cation lattice should change the spectra for those glasses in which the D_{4d} polytope is stabilized.

Magnetic Circular Dichroism Spectra. The MCD technique complements regular uv–visible spectral data by providing information about transitions to or from double degenerate excited states, which are indistinguishable from transitions between nondegenerate states using regular uv-visible spectroscopy. A detailed explanation of this phenomenon can be found in an excellent article by Schatz and McCaffery.[15]

Unfortunately, the MCD technique has limited functionality in the interpretations of the d-electron energy levels for the d^1 complexes, because every state is spin degenerate. For this reason each transition has associated *A*, *B*, and *C* terms, although one may predominate for a given transition. Therefore, the various electronic energy levels are indistinguishable *via* MCD, unless detailed calculations are performed on the system.

The aqueous solution MCD spectra of $Na_3[W(CN)_8]$ possess what appears to be an MCD *B* term centered at 23.7 kK not observed in the onium salt in acetonitrile (Table III). This difference in energy from 23.0 kK for the absorption peak is not within experimental error and implies that the MCD signal consists of *A*, *B*, and *C* term contributions as anticipated.

The MCD spectra of the $[M(CN)_8]^{4-}$ salts (M = Mo, W) are most easily interpreted because the octacyano d^2 systems are spin paired and have a nondegenerate $^1A_1$ ground state. Therefore, MCD *C* terms are eliminated and the degenerate d-orbital energy levels can be distinguishable from the nondegenerate levels by the presence of *A* terms in degenerate levels, unless the associated *B* terms are much more intense.[16]

For $[W(CN)_8]^{4-}$ the lowest energy MCD term observable is a *B* term at 19.6 kK. Although no transition is directly observed at this energy, gaussian analysis[8b] of the visible spectrum indicates a weak (ϵ 4.8) shoulder at 19.9 kK. Using the MCD value of 19.6 kK would not change the fit appreciably. The band was assigned as a weak spin-forbidden transition, $^3A_1 \leftarrow {}^1A_1$ previously.[8b] This singlet–triplet transition is allowed by the MCD $\Delta J = 1$ selection rule.

The next MCD signal is a definite *A* term having a negative *B* term superimposed. The distortion by the *B* term shifts the inflection point 0.3 kK from the position of the visible peak at 23.0 kK in the regular visible spectrum. The intensity of the transition (ϵ 110)[8b] and the MCD *A* term establish this transition as multiply degenerate, apparently $^1E \leftarrow {}^1A_1$ [*i.e.*, $(b_1)^1(e)^1 \leftarrow (b_1)^2$], establishing the lowest lying d-orbital excited state as a doubly degenerate energy level, even though most simplified calculations[8,17] have suggested that the ^1E level should be slightly higher than the $^1B_1$ level.

The transition at 27.0 kK also has an extinction coefficient (ϵ 251)[8b] which is typical of a d–d transition for a complex which does not contain a center of symmetry. The MCD term for this transition is a negative *B* term at the exact energy of the absorption and indicates that the transition is the nondegenerate $^1B_1 \leftarrow {}^1A_1$ [*i.e.*, $(b_1)^1(a_1)^1 \leftarrow (b_1)^2$], or possibly $^1A_2 \leftarrow {}^1A_1$ [*i.e.*, $(b_1)^1(b_2)^1$], although most calculations[8e,f,17] suggest that the $^1A_2$ level should be appreciably higher in energy.

The next MCD term appears to be a *B* term associated with the 33.0-kK transition reported previously,[8b] suggesting that the third spin-allowed d–d transition, $^1A_2 \leftarrow {}^1A_1$, occurs at this energy. The designation of this peak as a d–d transition between nondegenerate states is consistent with the extinction coefficient (520) of this peak. The reported extinction coefficients of $\geqslant$3000 for the higher energy terms indicate that they are charge-transfer transitions.

Analysis of the MCD spectrum of $[Mo(CN)_8]^{4-}$ in aqueous solution is in agreement with the conclusions reached for the tungsten analog. The lowest energy transition reported in the literature,[8b] at 19.6 kK, is spin forbidden on the basis of its low extinction coefficient (ϵ 2.7). The MCD spectrum shows a *B* term at 19.0 kK, although the regular visible spectrum obtained in this region shows only a flattened region in this vicinity from which a transition energy could not be ascertained with certainty.

By comparison to the $[Mo(CN)_8]^{4-}$ regular visible spectrum, the $^1E_1 \leftarrow {}^1A_1$ transition is expected to occur at 23.3 kK. However, the superposition of *A* and *B* terms causes this transition to appear as a flattened portion on the tail of

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(15) P. N. Schatz and A. J. McCaffery, *Quart. Rev., Chem. Soc.*, 552 (1969).

(16) R. L. Russell and B. E. Douglas, *Inorg. Chim. Acta*, 3, 426 (1969).

(17) (a) W. D. Bonds, Jr., R. D. Archer, and W. C. Hamilton, *Inorg. Chem.*, 10, 1764 (1971); (b) M. Randic and M. Vucelic, *J. Chem. Soc. A*, 3309 (1971). Naturally the possibility of a ^3E state at the same energy as a nondegenerate singlet (^1B, for example) cannot be absolutely ruled out, but the absence of even a hint of an "*A* term" for others of the next singlet levels supports our assignment.

the intense *B* term of the $^1B_1 \leftarrow {}^1A_1$ transition at 27.5 kK, analogous to the regular visible peak (27.3 kK). The remaining peaks are *B* terms for the $^1A_2 \leftarrow {}^1A_1$ transition at 35.8 kK and a charge-transfer peak at 41.3 kK.

An assignment of D_{2d} symmetry for aqueous $[W(CN)_8]^{4-}$ and $[Mo(CN)_8]^{4-}$ ions is logical and consistent with the MCD results, which verify Long and Vernon's vibrational spectroscopic conclusions.[7a]

Experimental Section

Solvents and Reagents. Ceric Sulfate (Matheson Coleman and Bell). A stock solution containing 0.1 *N* cerium(IV) and 1.8 *N* sulfuric acid was prepared according to Brown and Sallee.[18]

Potassium Permanganate (Baker). A stock solution of 0.101 *N* potassium permanganate was prepared by dissolving the salt in high-purity water. Because the permanganate anion is more stable in neutral or basic solutions than under acidic conditions, the stock solution was prepared in pure water and stored in the dark, as light is known to catalyze the decomposition of permanganate to manganese dioxide.[19] However, the solution to be titrated was made acidic (0.5 *N* with nitric acid) to allow the oxidation of the octacyanotungsten(IV) species to occur.

***N*-Phenylanthranilic Acid (Eastman).** A 0.005 *M* stock solution containing approximately one-tenth as much sodium carbonate was prepared following the procedure of Syrokomsky and Stiepin.[20]

Potassium chloride (Fisher), sodium chloride (Mallinckrodt), silver nitrate (Mallinckrodt), sodium carbonate (Fisher), tetra-*n*-butylammonium bromide (Eastman), anhydrous diethyl ether (Fisher), and 1-butanol (Fisher) were used without further purification. Water was purified using a Vaponics Control-o-Matic 200 water purification system to a conductivity of $\leqslant 0.1\ \mu\text{mho cm}^{-1}$.

Synthesis of the Octacyano Complexes. Potassium Octacyanotungstate(IV). A sample prepared by a standard procedure[21] was dissolved in a minimum amount of high-purity water, filtered, and allowed to recrystallize by slow evaporation of the water. The yellow powder was dried over potassium hydroxide before use in further syntheses or physical studies.

Anal. Calcd for $K_4[W(CN)_8]\cdot 2H_2O$: C, 16.4; H, 0.69; N, 19.2. Found:[22] C, 16.3; H, 0.90; N, 18.9.

Potassium Octacyanomolybdate(IV). A sample prepared by a standard procedure[23] was dissolved in a minimum amount of high-purity water, filtered, and precipitated by the addition of *ca.* 200 ml of ethanol. The powder was then washed with ethanol and dried *in vacuo* over calcium chloride for 2 days.

Anal. Calcd for $K_4[Mo(CN)_8]\cdot 2H_2O$: C, 19.4; H, 0.82; N, 22.6. Found: C, 19.2; H, 0.36; N, 22.6.

This and the other complexes have variable waters of hydration depending on the method of preparation and drying, although the dihydrate has been established as the stable hydrate for the potassium salt.

Sodium Octacyanotungstate(V). The synthetic scheme used in the preparation of hydrated $Na_3[W(CN)_8]$ was similar to that of Baadsgard and Treadwell.[24] Ceric sulfate was used as the oxidizing agent with *N*-phenylanthranilic acid as the indicator.[20]

Isopropyl alcohol was used to precipitate the product from solution. The orange-yellow powder was redissolved in a minimum amount of water and large columnar crystals were obtained upon slow evaporation of the solvent. The crystals were dried overnight over potassium hydroxide; yield 78%.

Anal. Calcd for $Na_3[W(CN)_8]\cdot 3H_2O$: C, 18.6; H, 1.16; N, 21.8. Calcd for $Na_3[W(CN)_8]\cdot 4H_2O$: C, 18.0; H, 1.50; N, 21.0. Found: C, 18.2; H, 1.29; N, 22.0. The ease of removal of the waters of hydration, noted by Bok, Leipoldt, and Basson,[4f] explains the difference in stoichiometry from the tetrahydrate species found for a single-crystal X-ray study by these authors.

Potassium Octacyanotungstate(V). The procedure used in the preparation of $K_3[W(CN)_8]\cdot H_2O$ was analogous to the method described for the sodium salt, replacing sodium chloride with potassium chloride.

Anal. Calcd for $K_3[W(CN)_8]\cdot H_2O$: C, 18.2; H, 0.38; N, 21.3. Found: C, 18.6; H, 0.76; N, 21.4.

Silver Octacyanotungstate(V). This salt was isolated as an intermediate in the preparation of the hydrated $Na_3[W(CN)_8]$. The red powder was washed well with water and dried *in vacuo* over potassium hydroxide overnight.

Anal. Calcd for $Ag_3[W(CN)_8]$: C, 13.4; H, 0.00; N, 15.7. Found: C, 13.6; H, 0.23; N, 15.6. The residual hydrogen was probably due to absorbed water.

Tetra-*n*-butylammonium Octacyanotungstate(V). The procedure used in the preparation of this salt was similar to the method used by Corden, Cunningham, and Eisenberg.[4e] $K_4[W(CN)_8]\cdot 2H_2O$ was oxidized in dilute nitric acid solution by 0.01 *N* potassium permanganate and the W(V) complex was precipitated by the addition of silver nitrate. After washing of the silver salt with several portions of water, the salt was dissolved in 3 *N* hydrochloric acid. The silver chloride was removed by filtration and excess tetra-*n*-butylammonium bromide was added to the filtrate, precipitating $[(n\text{-Bu})_4N]_3W(CN)_8$ as a white powder.

The powder was dissolved in a minimum amount of acetonitrile and ether was added until a turbidity was noticed. Then additional acetonitrile was added until the solution was again clear. Colorless square plates were obtained by slow evaporation of the solvent mixture.

Anal. Calcd for $[(n\text{-Bu})_4]_3W(CN)_8$: C, 60.2; H, 9.75; N, 13.8. Found: C, 60.0; H, 9.52; N, 14.1.

The colorless product slowly photodecomposed in the solid state to a red product, which was likewise soluble in acetonitrile. Further decomposition to a green species has not been noticed, although hydrated $Na_3[W(CN)_8]$ readily yielded a green product upon photodecomposition.

Spectral Studies. Electron Spin Resonance. The electron spin resonance spectra of the tungsten(V) octacyanide salts were recorded at ambient (+25°), liquid nitrogen (−196°), and liquid helium (−269°) temperatures on a Varian E-9 spectrometer. The esr signals were referenced to a sealed sample of *N,N*-diphenylpicrylhydrazyl contained in the auxiliary chamber of the dual resonant cavity. Spectra were interpreted following the procedure of Sands.[13] All samples were subjected to X-band microwave radiation; modulation frequency was 100-kHz microwave power varied from 0.5 to 10 mW; in general spectra were repeated at both ends of the range to ensure that all weak peaks were resolved as well as possible and that no signals were being saturated. The klystron frequency was 9.5 GHz at room temperature, 9.3 GHz at liquid nitrogen temperature, and 9.4 GHz at liquid helium temperature.

The powdered $Na_3W(CN)_8$ spectrum is actually an average composite of several spectra of the powdered sodium salt. Single spectra had artifacts because of nonrandom crystal orientations. Increasing the randomness of the microcrystals by increasing the volume of sample and introducing multiple reorientations of the sample tube resulted in eventual peak averaging. The other powders were finer and multiple spectra produced no changes.

Solution concentrations of $\sim 5 \times 10^{-3}\ M$ were used for the solution and glass spectra whenever possible. Aqueous solutions were measured in a specially designed cell to reduce broadening effects due to dipolar interactions. A matrix esr spectrum was also obtained with a 1% w/w powdered sample of the onium octacyanide in a $(n\text{-Bu})_4NBr$ matrix prepared by mixing solutions of each of the constituents dissolved in a minimum amount of acetonitrile and then rapidly removing the solvent under vacuum. Trace solvent was then removed by heating the sample to 100° *in vacuo* for 4 days in a drying pistol covered with aluminum foil to prevent photodecomposition of the octacyanide.

Electronic Absorption and Reflectance. Ultraviolet and visible absorption spectra of the salts were recorded on a Hitachi Model EPS-3T spectrophotometer and reflectance spectra were obtained with the addition of an integrating sphere accessory. Samples were investigated as 1,1,2,3,4,4-hexachlorobutadiene mulls between Supracil plates or as aqueous, acetonitrile, acetic acid, and 1-butanol solutions in matched 1.000-cm length Supracil cells with pure solvent in the reference beam. Spectral energies were calibrated with benzene in the near-infrared and ultraviolet regions and with didymium glass in the visible region.[25]

Magnetic Circular Dichroism. Room-temperature MCD studies

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(18) G. H. Brown and E. M. Sallee, "Quantitative Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963.

(19) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1967, pp 839–840.

(20) W. S. Syrokomsky and V. V. Stiepin, *J. Amer. Chem. Soc.*, **58**, 928 (1936). (See, however, R. Belcher and C. L. Wilson, "New Methods of Analytical Chemistry," Chapman and Hall, London, 1964, pp 34–36.)

(21) E. A. Heintz, *Inorg. Syn.*, **7**, 142 (1963).

(22) Analyses from the University of Massachusetts Division of Research Services Microanalytical Laboratory.

(23) N. H. Furman and C. O. Miller, *Inorg. Syn.*, **3**, 160 (1950).

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

were made with solutions of the tungsten and molybdenum species using the Cary 60 as modified by the Cary Division of Varian Instruments to accommodate a Varian superconducting magnet, employing a magnetic field of 44 kG. Samples and pure solvent were studied in 1- and 2-cm Supracil cells. Only spectral observations made for dynode voltages <400 V were considered as reliable. Spectra are base line corrected for solvent and cell absorptions.

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Registry No. $Na_3[W(CN)_8]$, 52239-56-2; $K_3[W(CN)_8]$, 18347-84-7; $[(n\text{-}Bu)_4N]_3[W(CN)_8]$, 52239-57-3; $K_4[W(CN)_8]$, 17475-73-9; $K_4[Mo(CN)_8]$, 17456-18-7; $Ag_3[W(CN)_8]$, 52239-58-4.

(25) Note Added in Proof. The spectrum recently reported as that of tetra-*n*-propylammonium octacyanotungstate(IV)[5d] is very similar to the spectra reported earlier for other salts of the tungstate(V) ion.[8] In fact, the tetra-*n*-propylammonium octacyanotungstate(V) salt has been isolated in our laboratory [C. J. Donahue, unpublished results] using the synthetic procedure[5d] for the "IV" salt. Apparently the octacyanotungstate(IV) ion is more susceptible to oxidation than the corresponding molybdenum complex; *e.g.*, the tungsten ion readily oxidizes in aqueous acid [A. Samotus and B. Kosowicz-Czajkowska, *Rocz. Chem.*, 45, 1623 (1971)].

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A Fourier Transform Carbon-13 Nuclear Magnetic Resonance Study of Thiocarbonyl and Other π-$(C_5H_5)M(CO)_2L$ Derivatives of Iron and Manganese

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^{13}C nmr spectra have been obtained for a series of complexes of the types π-$(C_5H_5)Cr(CO)_3^-$, π-$(C_5H_5)Mn(CO)_2L$ (L = CS, CO, $P(OPh)_3$, $P(OCH_3)_3$, PPh_3, PBu_3, $C_5H_{10}NH$, C_8H_{14}), and π-$(C_5H_5)Fe(CO)_2L^+$ (L = CS, CO, PPh_3, NH_3). The observed carbonyl chemical shift data are in agreement with a previously suggested hypothesis of increasingly deshielded carbonyl resonances with increasing transition metal → carbonyl π back-donation and suggest that the CS ligand is a significantly better π acceptor than CO in π-$(C_5H_5)Mn(CO)_2(CS)$. The thiocarbonyl in π-$(C_5H_5)Mn(CO)_2(CS)$ exhibits the most intensely deshielded carbon resonance yet reported. This would appear to indicate the localization of a substantial positive charge on the thiocarbonyl carbon atom, in close similarity to that suggested previously for the carbene carbon in $(CO)_5CrC(OCH_3)CH_3$.

Introduction

The characterization of transition metal-carbonyl complexes[1,2] preceded the first reports of analogous thiocarbonyl complexes by over 75 years.[3] While only a limited number of thiocarbonyl derivatives have been synthesized to date, their ubiquitous nature has been demonstrated by the characterization of complexes containing Rh,[3-6] Ir,[7-9] Ru,[10,11] Co,[12] Fe,[13,14] Mn,[15,16] Cr, Mo, and W,[17] and Ni, Pd, Pt, and Os.[18]

The relative scarcity of thiocarbonyl complexes does not arise from an inherent instability, but rather from synthetic complications. Thiocarbonyl complexes have been obtained *via* two synthetic schemes (eq 1 and 2) and thus depend either

$$\begin{aligned} &\pi\text{-}(C_5H_5)Fe(CO)_2^- + ClC(S)OR \rightarrow \pi\text{-}(C_5H_5)Fe(CO)_2C(S)OR \\ &\pi\text{-}(C_5H_5)Fe(CO)_2C(S)OR + HCl \rightarrow \pi\text{-}(C_5H_5)Fe(CO)_2(CS)^+ \end{aligned} \tag{1}$$

$$\begin{aligned} &(Ph_3P)_3RhCl + CS_2 \rightarrow (Ph_3P)_2RhCl(\pi\text{-}CS_2) \\ &(Ph_3P)_2RhCl(\pi\text{-}CS_2) + PPh_3 \rightarrow (Ph_3P)_2RhCl(CS) + S{=}PPh_3 \end{aligned} \tag{2}$$

upon the nucleophilicity of the starting material toward a derivative of thiophosgene or the relative stability of a transition metal-π-CS_2 intermediate.

Substantial evidence suggests that the CS ligand is a better π acceptor toward transition metals than its CO analog. Baird and Wilkinson[3] have argued that the absence of oxidative addition of HCl to $(Ph_3P)_2RhCl(CS)$ and the instability of this complex in the presence of $HgCl_2$ suggest the importance of a $(Ph_3P)_2ClRh^{\delta+}{=}C{=}S^{\delta-}$ resonance structure. This formulation is in accord with the crystallographic data of De Boer, *et al.*,[4] who found that the Rh-C bond length in $(Ph_3P)_2RhCl(CS)$ is 0.1 Å shorter than in $(Ph_3P)_2RhCl(CO)$, while the C-S bond length is only 0.018 Å shorter than the C=S bond length in CS_2. Yagupsky and Wilkinson[7] and Mays and Stefanini[9] have noted a reluctance of Ir-CS complexes to undergo oxidative addition with H_2 under conditions where their Ir-CO analogs undergo rapid reaction, and they have invoked an increased π acidity of the CS ligand to explain

(1) L. Mond, C. Langer, and F. Quinke, *J. Chem. Soc.*, 57, 749 (1890).
(2) L. Mond and C. Langer, *J. Chem. Soc.*, 59, 1090 (1891).
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