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Reactions of Eight-Coordinate Metal Cyanide Complexes. I. Molybdenum(IV) and Tungsten(IV) Oxocyanide Complexes

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The photohydrolysis products of $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$ have been characterized as six-coordinate oxocyanide complexes. Previous formulations of these products as eight-coordinate complexes are shown to be incorrect. The red $Na_4[MoO_2(CN)_4]\cdot 8H_2O$ and $K_4[MoO_2(CN)_4]\cdot 6H_2O$, yellow-brown $K_4[WO_2(CN)_4]\cdot 6H_2O$, blue $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$, and purple $K_3[WO(OH)(CN)_4]$ compounds were isolated and shown by X-ray diffraction, infrared spectroscopic, and chemical investigations to have two oxygen atoms *trans* to each other. The electronic spectra of these diamagnetic complexes are reported and their visible bands assigned. The spectroscopic studies indicate the existence of oxygen→metal and, to a lesser extent, metal→cyanide π bonding.

Introduction

Recent discussions of the bonding in eight-coordinate transition metal complexes[1-3] have emphasized the energetic similarities between the two most commonly occurring coordination polyhedra, the D_{4d} square antiprism and the D_{2d} dodecahedron.[4-6] Particular attention has been focused on ligand–ligand repulsion and crystal field stabilization energies. Unfortunately, since these energies are nearly identical for the two stereochemical configurations, it has not been possible to predict the preferred eight-coordination polyhedron for a given metal–ligand system.

In 1960, Orgel pointed out[7] that complexes of the type MX_4Y_4, where X is a good π-acceptor ligand and Y a poor π-acceptor ligand, might adopt the dodecahedral configuration. The reasoning behind this conclusion may be found in a number of articles.[1,3,5-7] In particular, it was suggested[7] that certain products of the photohydrolysis of $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$, which had previously been formulated[8] as $[Mo(CN)_4(OH)_4]^{4-}$ and $[W(CN)_4(OH)_4]^{4-}$, might have the four cyanide ligands situated at the four B vertices[1] of the dodecahedron.

In order to test experimentally the Orgel hypothesis, we have investigated the structural properties of the products obtained during the photolysis of aqueous solutions of $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$. Preliminary results[9] indicated that the red compound, previously obtained from these solutions upon addition of KOH and formulated[8,10] as "$K_4[Mo(OH)_4(CN)_4]\cdot 4H_2O$," was in fact $K_4[MoO_2(CN)_4]\cdot 6H_2O$. It was further suggested[9] that certain other photolysis products had also been incorrectly formulated as eight-coordinate.[8,10,11] Since little is known about transition metal oxocyanide complexes and since Mo(IV) and W(IV) compounds are relatively uncommon, we decided to carry out a thorough study of these ions. The results constitute the present report.

Experimental Section

All compounds were prepared from reagent grade materials. Potassium octacyanomolybdate(IV) was obtained by the method of Furman and Miller[12] in good yield. Potassium octacyanotungstate(IV) was prepared by the method of Adams,[13] but his reported yields could never be attained. The method of Mikhalevich and Litvinchuk[14] was subsequently found to be preferable.

Photolysis reactions were carried out using a 450-w Hanovia medium-pressure mercury-arc lamp. Solutions were contained in Pyrex reaction vessels which filter out essentially all radiation of wavelengths less than 3000 A.

Metal analyses were performed by oxidation of the metals with boiling aqua regia to the hexavalent state followed by precipita-

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[1] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).
[2] D. L. Kepert, *J. Chem. Soc.*, 4736 (1965).
[3] R. V. Parish and P. G. Perkins, *ibid.*, 345 (1967).
[4] E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).
[5] R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966).
[6] S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).
[7] L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960).
[8] V. Carassiti, A. M. Marinangeli, and V. Balzani, *Ann. Chim.* (Rome), **50**, 806 (1960), and references contained therein.
[9] S. J. Lippard, H. Nozaki, and B. J. Russ, *Chem. Commun.*, 118 (1967).
[10] W. Jakób and Z. Jakób, *Roczniki Chem.*, **36**, 601 (1962), and references contained therein.
[11] A. W. Adamson and J. R. Perumareddi, *Inorg. Chem.*, **4**, 247 (1965).
[12] N. H. Furman and C. O. Miller, *Inorg. Syn.*, **3**, 160 (1950).
[13] A. C. Adams, Ph.D. Thesis, University of Wisconsin, 1965.
[14] K. N. Mikhalevich and V. N. Litvinchuk, *Russ. J. Inorg. Chem.*, **4**, 800 (1959).

tion as the oxinates.[15] Organic microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Some difficulty was experienced in getting good C and N analyses, as has been observed by other workers for similar compounds.[16]

Potassium Dioxotetracyanomolybdate(IV) Hexahydrate, $K_4[MoO_2(CN)_4]\cdot 6H_2O$.—(A) A modification of the method of Bucknall and Wardlaw[17] was used. A 10% solution of MoO_3 in 4 *N* HCl (250 ml) contained in a porous pot was reduced electrolytically at a platinum cathode. The porous pot was surrounded by a 1-l. beaker containing 400 ml of a saturated KCl solution and a graphite anode. The current (6 v, 4 amp) was switched off when addition of alkali to an aliquot of the catholyte produced a light brown precipitate (~90 min). Further reduction gave a red-brown solution which produced only a black precipitate when made alkaline. This black precipitate was much less soluble in aqueous KCN solution. The brown precipitate obtained by the addition of base as suggested above was dissolved in the minimum amount (~100 ml) of aqueous KCN (4 *M*) to give a blue or green solution. The green solution was made blue by the addition of KOH. The addition of further solid KOH precipitated red crystals which were filtered, washed with alcohol and ether, and dried in air; yield, 25 g (45%). *Anal.* Calcd for $K_4[MoO_2(CN)_4]\cdot 6H_2O$: C, 9.68; H, 2.42; N, 11.29. Found: C, 10.45; H, 2.61; N, 11.63.

(B) The compound was also obtained by the photolysis of $K_4[Mo(CN)_8]$.[10] Irradiation of 5 g of the octacyanide in 100 ml of water gave, after 8 hr, a blue solution which was treated as above; yield, 4.5 g (90%). *Anal.* Calcd: Mo, 19.32. Found: C, 9.62; H, 2.60; N, 10.93; Mo, 19.0. The red crystals slowly turned blue in the atmosphere. They could be stored in a stoppered bottle without noticeable change.

Potassium Dioxotetracyanotungstate(IV) Hexahydrate, $K_4[WO_2(CN)_4]\cdot 6H_2O$.—(A) Following the directions of Mikhalevich and Litvinchuk,[14] the compound could be prepared electrolytically in ~25% yield. *Anal.* Calcd for $K_4[WO_2(CN)_4]\cdot 6H_2O$: C, 8.21; H, 2.07; N, 9.57; W, 31.41. Found: W, 31.4.

(B) The photolysis of $K_4[W(CN)_8]$[10] was also used to prepare the compound in 90% yield. *Anal.* Found: C, 9.17; H, 2.04; N, 10.20. The yellow-brown crystals slowly turned purple in a moist atmosphere.

Sodium Dioxotetracyanomolybdate(IV) Octahydrate, $Na_4[MoO_2(CN)_4]\cdot 8H_2O$.—A 0.1 *M* aqueous solution of sodium octacyanomolybdate(IV) (50 ml) was made by adding a sodium perchlorate solution to potassium octacyanomolybdate(IV) and removing precipitated potassium perchlorate by filtration. The solution was photolyzed as for the potassium salt (method B above) and red crystals precipitated by addition of solid NaOH to the blue solution; yield, 3.5 g (~70%). *Anal.* Calcd for $Na_4[MoO_2(CN)_4]\cdot 8H_2O$: C, 10.26; H, 3.45; N, 11.97. Found: C, 10.93; H, 3.47; N, 11.97.

Potassium Oxohydroxotetracyanomolybdate(IV) Dihydrate, $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$.—Bucknall and Wardlaw[17] isolated a blue solid from the blue solution obtained in method A for preparing $K_4[MoO_2(CN)_4]\cdot 6H_2O$ by adding alcohol. We experienced difficulty with this method, an oil being the usual product. Instead, when 5 g of red $K_4[MoO_2(CN)_4]\cdot 6H_2O$ was treated with 75 ml of methanol, it rapidly turned blue. The royal blue product was filtered off and air dried; yield, 3.8 g (98%). *Anal.* Calcd for $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$: C, 12.43; H, 1.30; N, 14.51. Found: C, 12.26; H, 0.73; N, 14.51.

Potassium Oxohydroxotetracyanotungstate(IV), $K_3[WO(OH)(CN)_4]$.—Following a procedure analogous to the preparation of the corresponding molybdenum complex described above, $K_4[WO_2(CN)_4]\cdot 6H_2O$ gave a purple product in 97% yield when treated with methanol. *Anal.* Calcd for $K_3[WO(OH)(CN)_4]$: C, 10.96; H, 0.23; N, 12.78; W, 42.01. Found: C, 11.94; H, 0.58; N, 12.72; W, 41.8.

Dehydration Experiments.—Weighed samples of the complexes (~0.1 g) were heated *in vacuo* to ~110° for several hours. The following results were noted. $K_4[MoO_2(CN)_4]\cdot 6H_2O$ quickly turned yellow and lost 21.7% of its weight (expected loss for six water molecules, 21.8%). $K_4[WO_2(CN)_4]\cdot 6H_2O$ became a slightly lighter shade of yellow and lost 18.2% of its weight (expected loss for six water molecules, 18.5%). $K_3[MoO(OH)(CN)_4]\cdot 6H_2O$ became a slightly darker shade of blue and lost varying percentages by weight, the greatest being 9.1% (expected loss for two water molecules, 9.3%). $K_3[WO(OH)(CN)_4]$ did not change color and lost less than 0.3% of its weight.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer as Nujol mulls or as aqueous solutions contained in zinc polysulfide cells. Visible and ultraviolet spectra of solutions were run at concentrations of approximately 10^{-2} to 10^{-4} *M* on a Cary Model 14 recording spectrometer using 1.0-cm matched quartz cells. Solid-state ultraviolet–visible spectra were taken of Nujol mulls supported on strips of absorbent paper in modified cell holders for the Cary 14. Magnetic susceptibilities were measured by the Gouy method at room temperature. Single-crystal X-ray diffraction data were collected on Weissenberg and precession cameras using Cu Kα radiation. Densities were determined by flotation in suitable mixed organic liquids.

Results

Single-Crystal X-Ray Studies.—Crystals of $K_4[MoO_2(CN)_4]\cdot 6H_2O$ and $K_4[WO_2(CN)_4]\cdot 6H_2O$ were easily obtained from concentrated KOH solutions as needles developed along *a*. Prismatic forms could be obtained by very slow growth. Single-crystal X-ray diffraction studies of the molybdenum complex indicated the space group to be the monoclinic $P2_1/c$, with $a = 7.23 \pm 0.01$, $b = 13.48 \pm 0.01$, $c = 9.35 \pm 0.01$ A, $\beta = 113°\ 45'$. From the experimentally determined density, $\rho = 1.95 \pm 0.01$ g/cc, the number of formula units per unit cell was fixed at two ($\rho_{\text{calcd}} = 1.97$ g/cc). The tungsten complex was subsequently found to have identical cell constants (no more than 0.5% different), with the relative intensities of comparable reflections being quite similar. The two compounds are therefore considered to be isostructural. The space group $P2_1/c$ requires that the two heavy-metal atoms in the unit cell occupy centers of inversion. There was no evidence for disorder on any of the photographs.

Infrared Spectra.—The infrared spectra in the frequency regions where cyanide stretching, metal–oxygen stretching, and out-of-plane M–O–H deformation modes usually occur are summarized for each complex in Table I. The assignment of the out-of-plane M–O–H deformation mode was checked for M = Mo by dissolving the red $K_4[MoO_2(CN)_4]\cdot 6H_2O$ in D_2O to form a blue solution which was evaporated to give a blue powder, presumably $K_3[MoO(OD)(CN)_4]\cdot 2D_2O$. The spectrum of this compound showed no band at 1057 cm^{-1}. Instead, a new band appeared at 822 cm^{-1} which we tentatively assign to the Mo–O–D deformation mode. In addition to the peaks listed in Table I, each spectrum had the characteristic O–H stretching and H–O–H bending frequencies expected for strongly hydrogen-bonded lattice water. The only exception was $K_3[WO(OH)(CN)_4]$, for which no water bending mode at ~1600 cm^{-1} could be discerned. The spectra of the dioxotetracyanometalates also showed weak

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[15] A. I. Vogel, "Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., New York, N. Y., 1948, p 523.

[16] C. J. L. Lock and G. Wilkinson, *J. Chem. Soc.*, 2281 (1964).

[17] W. R. Bucknall and W. Wardlaw, *ibid.*, 2981 (1927).

TABLE I

SUMMARY OF INFRARED SPECTRAL BANDS AND ASSIGNMENTS[a]

Compound[b]	$\nu(C\equiv N)$, cm^{-1}	$\delta(M-O-H)$, cm^{-1}	$\nu(M=O)$, cm^{-1}
$K_4[MoO_2(CN)_4]\cdot 6H_2O$	2060 s	...	800 vb
$Na_4[MoO_2(CN)_4]\cdot 8H_2O$	2075 s	...	850–790 vvb
$K_4[WO_2(CN)_4]\cdot 6H_2O$	2060 s	...	720 vb
$K_3[MoO(OH)(CN)_4]\cdot 2H_2O$	2095 s	1057 m	921 s
	2060 s[c]	...	
$K_3[MoO(OD)(CN)_4]\cdot 2D_2O$	2090 s	822 s?	920 s
$K_3[WO(OH)(CN)_4]$	2075 s	1072 m	875 s

[a] Values reported are accurate to ±5 cm^{-1}. Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad. [b] All spectra taken of Nujol mulls unless otherwise indicated. [c] Aqueous solution.

absorptions at 2170 and 2270 cm^{-1}, but these are probably too high in energy to result from complexed cyanide groups.[18] No other important bands were observed in the 4000–650-cm^{-1} region investigated.

Visible and Ultraviolet Spectra.—Table II presents the results obtained for the four complex anions. Solution spectra could not be obtained for the $[MO_2(CN)_4]^{4-}$ species, as these are immediately hydrolyzed to $[MO(OH)(CN)_4]^{3-}$ ions. Typical spectra for the Nujol suspensions of the four species are displayed in Figure 1.

TABLE II

SUMMARY OF ELECTRONIC SPECTRAL BANDS

Compound	Freq,[a] cm^{-1}	Molar extinction coeff[b]
$K_4[MoO_2(CN)_4]\cdot 6H_2O$	19,050	w
$K_3[MoO(OH)(CN)_4]\cdot 2H_2O$	16,900	38.7
	44,450	19,900
	46,500	~17,000 sh
$K_3[MoO(OH)(CN)_4]\cdot 2H_2O$	16,950	w
$K_4[WO_2(CN)_4]\cdot 6H_2O$	21,300	w
$K_3[WO(OH)(CN)_4]$	18,600	59
	32,800	~ 1,200 sh
	42,200	19,000
$K_3[WO(OH)(CN)_4]$	19,250	w

[a] Nujol suspensions observable out to 40,000 cm^{-1}. [b] No entry given for Nujol suspensions. Abbreviations: w, weak; sh, shoulder.

Magnetic Susceptibilities.—The room-temperature molar susceptibilities, uncorrected for underlying metal diamagnetism, were found to be -100×10^{-6} cgs unit/mole for $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$, -23×10^{-6} cgs unit/mole for $Na_4[MoO_2(CN)_4]\cdot 8H_2O$, 10^{-6} cgs unit/mole for $K_4[WO_2(CN)_4]\cdot 6H_2O$, and -18×10^{-6} cgs unit/mole for $K_3[WO(OH)(CN)_4]$. Thus all complexes are diamagnetic.

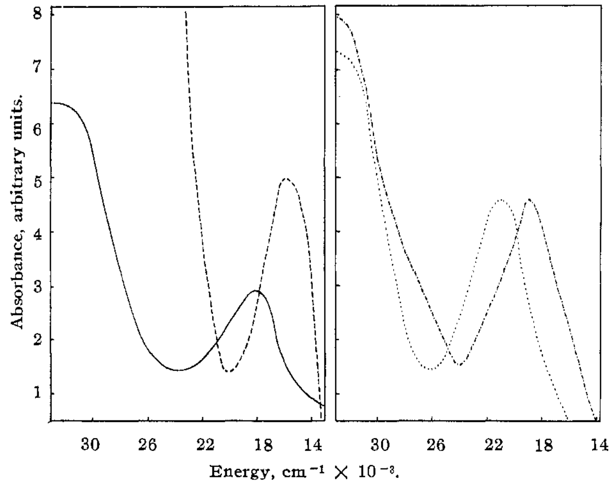

Figure 1.—Visible spectra of Nujol suspensions of $K_4[MoO_2(CN)_4]\cdot 6H_2O$ (———), $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$ (– – – –), $K_4[WO_2(CN)_4]\cdot 6H_2O$ (· · · ·), and $K_3[WO(OH)(CN)_4]$ (— · — · — ·).

Chemical Interconversion of the Red and Blue Products.—On exposure to the atmosphere, the red or yellow-brown dioxotetracyanometalates slowly take up moisture and turn blue (for Mo) or purple (for W), respectively. This conversion was investigated for the red molybdenum crystals, which reacted with absolute methanol and methanol–water (9:1) to form a blue powder. At intermediate water concentrations (90% ≤ concentration of CH_3OH ≤ 100%), the red → blue conversion occurred less readily. No reaction was observed with absolute or 95% ethanol. Bucknall and Wardlaw report[17] that the conversion can also be accomplished by carefully dehydrating the red complex. Following their procedure, $K_4[MoO_2(CN)_4]\cdot 6H_2O$ was dried in a desiccator over concentrated H_2SO_4. Most of the crystals became dull green and a few turned yellow-green. In view of this behavior, the products were not investigated further.

Discussion

Chemical and Structural Properties.—The strongest evidence for the structural assignment of the red molybdenum and yellow-brown tungsten photohydrolysis products as *trans*-dioxotetracyanometalate(IV) complexes comes from the X-ray diffraction results, which require the metal atoms to occupy centers of inversion. If the metal atoms were eight-coordinate, as prescribed by the tetrahydroxotetracyanometalate(IV) formulation, the complexes would have to exhibit cubic or hexagonal bipyramidal coordination.[6] Since these coordination polyhedra are virtually unknown for transition metal complexes, it is very unlikely that they occur for the present compounds.

The formulation of $K_4[MoO_2(CN)_4]\cdot 6H_2O$ and $K_4[WO_2(CN)_4]\cdot 6H_2O$ has further been verified by dehydration experiments, in which, at 110° *in vacuo*, each compound was observed to lose almost exactly the required amount of weight for six water molecules of hydration. In addition, examination of the infrared spectra of the two complexes reveals a broad, intense band around 800 cm^{-1}, a region in which *trans* O–M–O groups are commonly thought to occur.[19] The unusual breadth of the bands (~150 cm^{-1}) may be ascribed to extensive hydrogen bonding between the lattice water protons and the oxo ligands.

A careful study of the hydrolysis of the red $K_4[MoO_2(CN)_4]\cdot 6H_2O$ crystals to produce the blue prod-

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(18) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 166 ff.

(19) *Cf.* W. P. Griffith and T. D. Wickens, *J. Chem. Soc., Sect. A*, 674 (1967), and references contained therein.

uct, $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$, indicates that the latter may be formed by either of two distinct pathways: (a) by direct hydrolysis of the red compound, which occurred in solutions where the $H_2O:CH_3OH$ ratio was $\geqslant 10\%$, and (b) by dehydrative hydrolysis, when absolute methanol was used. The second process may be represented as the intramolecular hydrolysis

$$K_4[MoO_2(CN)_4]\cdot 6H_2O \longrightarrow K_3[MoO(OH)(CN)_4]\cdot 2H_2O + KOH + 3H_2O$$

involving a water molecule which is almost certainly hydrogen bonded to the MoO_2 unit. This interpretation is compatible with the infrared evidence for hydrogen bonding mentioned above.

The chemical and structural characterization of the blue molybdenum and purple tungsten solids as *trans*-oxohydroxotetracyanometalate(IV) species has been achieved by the complementary use of chemical analysis, dehydration experiments, and infrared spectroscopy. Previous workers have formulated the molybdenum compound as $K_3[Mo(CN)_4(OH)_3(H_2O)]$[11] or $K_2[Mo(CN)_4(OH)_2]$,[10] and it remains to be proved that neither formulation can explain all of the data.

The formula $K_2[Mo(CN)_4(OH)_2]$ has been discounted[11] on the grounds that it would require analytical figures which disagree with those found. Our results support this conclusion. Analytically it is impossible to distinguish between the eight-coordinate formulation,[11] $K_3[Mo(CN)_4(OH)_3(H_2O)]$, and our six-coordinate formulation, $K_3[MoO(OH)(CN)_4]\cdot 2H_2O$, however. Strong support for the latter is obtained (a) by analogy to the structurally characterized $[MoO_2(CN)_4]^{4-}$ ion, (b) from a dehydration experiment in which the complex was observed to lose weight corresponding to the loss of two waters of hydration, and (c) from infrared spectral studies. As indicated in Table I, a strong band at 921 cm^{-1} in the infrared spectrum of the solid blue photoproduct may be assigned to an Mo=O stretching mode. A corresponding peak is found in the spectrum of $K_3[WO(OH)(CN)_4]$ at 875 cm^{-1}. Assuming that the force constants are about the same, the relative frequencies should be dictated by the square root of the relative reduced masses of the M–O units. Accordingly, we calculate that the tungsten–oxygen stretching frequency should occur at 868 cm^{-1}, in good agreement with the observed value. The peaks at 1057 and 1072 cm^{-1} in the infrared spectra of $[MoO(OH)(CN)_4]^{3-}$ and $[WO(OH)(CN)_4]^{3-}$, respectively, are assigned to out-of-plane M–O–H deformation modes (Table I).[20] This assignment was verified by a deuterium-labeling experiment. A final piece of evidence for the $[MO(OH)(CN)_4]^{3-}$ rather than the $[M(CN)_4(OH)_3(H_2O)]^{3-}$ formulation is the very existence of the anhydrous salt, $K_3[WO(OH)(CN)_4]$. Noteworthy is the attempted dehydration of this deep purple complex, which neither changed color nor lost weight upon heating for 24 hr *in vacuo* at 110°.

As indicated in the Experimental Section, the molybdenum(IV) and tungsten(IV) oxocyanide complexes can also be prepared[14,17,21] from electrochemically produced, quinquevalent molybdenum and tungsten hydroxides. We have verified that, with respect to all of their physical and chemical properties, these complexes are identical with the compounds obtained photochemically. Analogous *trans*-dioxorhenium(V)[22] and -osmium(VI)[23] complexes, $[ReO_2(CN)_4]^{3-}$ and $[OsO_2(CN)_4]^{2-}$, are also known, the potassium salt of the former having been structurally characterized in an X-ray diffraction study.[22d] Acid hydrolysis of these complexes is generally assumed to produce tetrahydroxotetracyanometalates by analogy to the "well known Mo and W compounds."[24] The present work clearly indicates that these hydrolysis products are more likely $[MO(OH)(CN)_4]^{n-}$ or perhaps $[M(OH)_2(CN)_4]^{n-}$ ions, as has been suggested by other workers.[6] Attempts on our part to precipitate a $[Mo(OH)_2(CN)_4]^{2-}$ species by addition of acid to the blue solution of $[MoO(OH)(CN)_4]^{3-}$ have thus far been unsuccessful. Apparently, an acid hydrolysis occurs with the loss of cyanide as HCN. The resultant green solution was not further characterized.[24a]

Electronic Structure and Spectra.—Under D_{4h} symmetry, the complexes $[MoO_2(CN)_4]^{4-}$ and $[WO_2(CN)_4]^{4-}$ require a set of $2a_{1g}$ (s + d_{z^2}) + a_{2u} (p_z) + b_{1g} ($d_{x^2-y^2}$) + e_u (p_x,p_y) metal atom orbitals for σ bonding. We assume by analogy to other transition metal oxo complexes[25] that considerable oxygen to metal π bonding, involving the metal e_g (d_{xz},d_{yz}) orbitals, occurs in these molecules. It is therefore reasonable to place the two metal d electrons into an approximately nonbonding (*vide infra*) d_{xy} orbital. This electronic configuration gives rise to a $^1B_{2g}$ ground state, which is consistent with the observed diamagnetism. In the absence of an inversion center, only one d–d transition, $b_2^2 \rightarrow b_2e$, would be symmetry allowed. Since there is only one prominent band in the visible spectrum of each of the two dioxo complexes (Figure 1), we assign it to the spin-allowed $^1B_{2g} \rightarrow {}^1E_g$ transition. The apparent relaxation of the Laporte selection rule here may possibly result from vibronic coupling.

It is useful at this point to refer to the molecular orbital calculation of Gray and Hare[25a] for the $[MoOCl_5]^{2-}$ ion, in which a band at 13,800 cm^{-1} was assigned to the $^2B_2 \rightarrow {}^2E$ transition. Qualitatively, the separation

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[20] See ref 18, p 155 ff.

[21] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 873 (1959).

[22] (a) W. Klemm and G. Frischmuth, *Z. Anorg. Allgem. Chem.*, **230**, 215 (1937); (b) G. T. Morgan, *J. Chem. Soc.*, 568 (1953); (c) G. T. Morgan and G. R. Davies, *ibid.*, 1858 (1938); (d) K. Lukaszewicz and T. Glowiak, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, **9**, 613 (1961).

[23] F. Krauss and G. Schrader, *J. Prakt. Chem.*, **120**, 36 (1928).

[24] M. H. Ford-Smith, "The Chemistry of Complex Cyanides," Her Majesty's Stationery Office, London, 1964, p 56.

[24a] Note Added in Proof.—Recent work by Mr. M. Kronstadt in our laboratory has led to the successful synthesis and characterization of the green compound, $[(C_6H_5)_4As]_2[Mo(OH)_2(CN)_4]$. We also call the reader's attention to the recent report (V. Day and J. L. Hoard, American Crystallographic Association Meeting, Minneapolis, Minn., 1967, Abstracts, p 75) of the crystal structure of $K_3Na[MoO_2(CN)_4]\cdot 6H_2O$, which further corroborates the structural assignments made in the present paper.

[25] (a) H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962), and references contained therein; (b) F. A. Cotton and S. J. Lippard, *ibid.*, **5**, 416 (1966), and references contained therein.

between the metal d_{xy} and degenerate, antibonding d_{xz}, d_{yz} (e_π*) orbitals in $[MoO_2(CN)_4]^{4-}$ will differ from the corresponding energy level separation in $[MoOCl_5]^{2-}$ in the following manner. First, the presence of a second π-electron donor oxygen atom will tend to raise the e_π* level. In addition, the energetically accessible antibonding π orbitals of the cyanide ligands can both (1) accept some electron density from the d_{xy} metal orbital, thereby lowering the nonbonding b_{2g} energy level, and (2) lower the e_π* energy level by removing electrons from the e_π bonding MO, thereby raising its energy. Without carrying out a complete MO calculation, one cannot predict the relative effects of these various possibilities. From the energy (19,050 cm^{-1}) of the $^1B_{2g} \rightarrow {}^1E_g$ transition in $[MoO_2(CN)_4]^{4-}$, however, it appears that the raising of the e_π* by the second oxygen atom has had the greatest effect.

This analysis may also be applied in a consistent way to the diamagnetic oxohydroxo complexes, which may be thought to have a $^1B_2$ ground state. In the visible spectrum of $[MoO(OH)(CN)_4]^{3-}$ there is a single band at 16,900 cm^{-1}, which we assign to the $^1B_2 \rightarrow {}^1E$ transition. A corresponding spectral transition occurs for the $[WO(OH)(CN)_4]^{3-}$ complex (Table II and Figure 1). In the oxohydroxo complexes, the π-donor ability of one of the oxygen atoms has been greatly reduced by protonation, and the energy of the e_π* level is correspondingly lower. This explains the observed red shifts (Figure 1). The lowering of the b_2 (d_{xy}) orbital by the cyanide ligands can still occur, moreover, and this may be the reason why the $^1B_2 \rightarrow {}^1E$ transition is 4000 cm^{-1} higher in energy for $[MoO(OH)(CN)_4]^{3-}$ than for $[MoOCl_5]^{2-}$.

The above arguments provide a reasonable explanation for the pronounced color changes accompanying the $[MO_2(CN)_4]^{4-} \rightarrow [MO(OH)(CN)_4]^{3-}$ conversion, where M is molybdenum or tungsten. No attempt will be made at present to assign the other bands observed in the ultraviolet region of the spectrum of aqueous solutions of the $[MO(OH)(CN)_4]^{3-}$ ions (Table II). From the close correspondence in the positions of the visible bands in the solid-state and solution spectra of these complexes (Table II), we conclude that they have identical structures in both media. The molar extinction coefficients of these bands are characteristic of the d → d transitions to which they have been assigned.

One final comment concerning the infrared spectra of the various complex ions in the C≡N stretching frequency region is in order. For $[MoO_2(CN)_4]^{4-}$ and $[WO_2(CN)_4]^{4-}$, a single sharp band was observed at 2068 cm^{-1} (average for the sodium and potassium salts) and 2060 cm^{-1}, respectively. This is in accord with the known D_{4h} symmetry. In the oxohydroxotetracyanometalates, however, where the symmetry (ignoring the hydroxyl proton) is C_{4v}, two infrared-active bands are predicted but only one shows up (Table I). We assign this to the E mode, since the A_1 mode would be expected to be much less intense. Of interest is the fact that the cyanide stretching frequencies occur at higher energies for $[MoO(OH)(CN)_4]^{3-}$ (2095 cm^{-1}) and $[WO(OH)(CN)_4]^{3-}$ (2075 cm^{-1}) than for the corresponding dioxo complexes. This result suggests that metal–cyanide back-bonding is greater for complexes containing the O–M–O group than for the oxohydroxo complexes, as one might predict. These comments are not inconsistent with our previous discussion of the electronic spectra, although direct comparisons are not too meaningful in the absence of more quantitative calculations.

Concluding Remarks

The failure to obtain the eight-coordinate $[M(OH)_4(CN)_4]^{4-}$ ions in the photochemical reactions of aqueous solutions of $[M(CN)_8]^{4-}$ leaves Orgel's prediction[7] as yet unproved. From the present work it appears that the tendency for Mo(IV) and W(IV) to form multiple bonds with oxygen will prevent the formation of suitable test compounds in aqueous solutions. Photochemical studies of $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$ in nonaqueous media are currently in progress in our laboratory in an attempt to eliminate this problem.

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