we are dealing with spectra of solids at low temperature, in which the anion does not necessarily behave ideally, it is possible that the symmetric stretching vibration of ClF_4^- might have become infrared active. The presence of this vibration may be due to either distortion of the square-planar ClF_4^- anion (thus lowering the symmetry from D_{4h} to C_{4v}) or to a crystal lattice effect. Then the assignments could be made in analogy to the vibrations of the square-planar ClF_4 part of the ClF_5 molecule.[18] However, the found intensities do not agree so well with this assignment. The planar *trans*-XY_2Z_2 structure is also possible. In this case, the band at 498 cm^{-1} would be a deformation vibration. However, the band at 541 cm^{-1} is asymmetric, and most infrared spectra of $NO^+ClF_4^-$ showed a very weak shoulder at 570 cm^{-1}. On the basis of this and the fact that the position of the band at 498 cm^{-1} does not exclude its interpretation as a stretching vibration, the possibility of assigning the ClF_4^- anion in $NO^+ClF_4^-$ to the point group C_{2v} cannot be eliminated. Regardless, the symmetry of the ClF_4^- anion in $NO^+ClF_4^-$ at low temperature appears to be lower than D_{4h} (found for $RbClF_4$ and $CsClF_4$).

Conclusion

(i) The ionic structure, $NO^+ClF_4^-$, is assigned to the 1:1 adduct formed from NOF and ClF_3. (ii) The tetrafluorochlorate(III) anion in $RbClF_4$ and $CsClF_4$ has square-planar (symmetry D_{4h}). (iii) The tetrafluorochlorate(III) anion in $NOClF_4$ at low temperature has lower symmetry than D_{4h}. (iv) The square-planar structure found for the ClF_4^- anion in $RbClF_4$ and $CsClF_4$ is in agreement with either the semiempirical molecular orbital model, assuming semiionic bonds, or the sp^{3}d^2-hybridization model. (v) Since $KClF_4$ and $KBrF_4$ are isostructural according to their X-ray data, the interpretation of $KBrF_4$ in terms of a planar rather than a tetrahedral BrF_4^- anion seems more likely.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Structure of the Octacyanomolybdate(V) and -tungstate(V) Ions from Electron Spin Resonance[1]

BY B. R. McGARVEY

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The anisotropic spin Hamiltonian parameters of the $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ ions have been determined from the esr spectra of frozen glycerine solutions. The results can be interpreted as showing that the ions possess the Archimedean antiprism structure in solutions. The g values for ions in the duodecahedral configuration have also been obtained from esr spectra of the ions trapped in the crystal lattice of $K_4Mo(CN)_8$ and $K_4W(CN)_8$. The magnitude of the spin Hamiltonian parameters shows that there is considerable covalency in the metal–cyanide bonds.

Introduction

The structure of eight-coordinated ions has been of interest for some time. On the basis of X-ray diffraction studies, Hoard and Nordsieck[2] found the structure of $Mo(CN)_8^{4-}$ to be duodecahedral in the crystal $K_4Mo(CN)_8 \cdot 2H_2O$. Stammreich and Sala[3] found, however, that Raman and infrared data support an Archimedean antisprism structure for the same ion when in solution. There have been no determinations of the structure of the paramagnetic ions $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$. The optical spectra of octacyanide complexes of Mo(IV), Mo(V), W(IV), and W(V) have been determined[4-7] but have been of little value in determining structure. In fact they have been interpreted theoretically in terms of both the duodecahedral structure[4] and the antiprism structure.[7,8] The esr of powders of $K_3Mo(CN)_8$, $K_3W(CN)_8$, $Ag_3Mo(CN)_8$, and $Ag_3W(CN)_8$ have been determined[8,9] as well as the esr of aqueous solutions[10,11] of the $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ ions. However there have been no reports on the anisotropic components of the spin Hamiltonian.

Experimental Section

The compounds $K_4Mo(CN)_8$ and $K_4W(CN)_8$ were prepared using procedures given in *Inorganic Syntheses*.[12] Aqueous solu-

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[1] This work was supported by NSF Grant GP-4215.

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[11] S. I. Weissman and C. S. Garner, *J. Am. Chem. Soc.*, **78**, 1072 (1956).

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TABLE I

SPIN HAMILTONIAN PARAMETERS FOR $Mo(CN)_8^{3-}$ AND $W(CN)_8^{3-}$.

Ion	Solvent	T, °K	$g_\parallel$	$g_\perp$	$\langle g \rangle$	A (10^{-4} cm^{-1})	B (10^{-4} cm^{-1})	$\langle A \rangle$ (10^{-4} cm^{-1})	$\langle A \rangle$ (C^{13}) (10^{-4} cm^{-1})
$Mo(CN)_8^{3-}$	Water	298			1.9915 ± 0.0005			30.3 ± 0.1	10.9 ± 0.2
	Glycerine	77	1.9981 ± 0.0005	1.9889 ± 0.0005	1.9920 ± 0.0005	14 ± 2	39.1 ± 0.4	30.7 ± 0.8	
	$K_4Mo(CN)_8$	298	1.9779 ± 0.0006	1.9882 ± 0.0005	1.9848 ± 0.0005				
$W(CN)_8^{3-}$	Water	298			1.9706 ± 0.0010			51.9 ±0.5	
	Glycerine	77	1.9819 ± 0.0010	1.9677 ± 0.0010	1.9724 ± 0.0010	(18.7)	68.5 ±0.6	(5.19)	
	$K_4W(CN)_8$	298	1.942 ± 0.010	1.973 ± 0.002	1.963 ± 0.005				

tions of $K_3Mo(CN)_8$ and $K_3W(CN)_8$ were prepared by first titrating a water solution of $K_4Mo(CN)_8$ or $K_4W(CN)_8$ with $KMnO_4$. $AgNO_3$ was then added to precipitate $Ag_3Mo(CN)_8$ or $Ag_3W(CN)_8$. The precipitate was washed with water and then added to a solution of KCl. The resulting AgCl was filtered off, leaving a solution of $K_3Mo(CN)_8$ or $K_3W(CN)_8$. The glycerine solutions were obtained by adding one part of an aqueous solution of $K_3Mo(CN)_8$ or $K_3W(CN)_8$ to nine parts of glycerine.

The esr spectra were obtained with a Varian V-4500 spectrometer employing 100 kc/sec modulation. The spectra were calibrated using an Alpha Scientific AL67 nmr field meter. The klystron frequency was 9.5 kMc/sec for room temperature measurements and 9.1 kMc/sec for liquid nitrogen measurements.

Results

The esr spectra of aqueous solutions of both $K_3Mo(CN)_8$ and $K_3W(CN)_8$ were obtained and fitted to the spin Hamiltonian

$$\mathcal{H} = \langle g \rangle \beta \mathbf{H} \cdot \mathbf{S} + \langle A \rangle \mathbf{I} \cdot \mathbf{S} \qquad (1)$$

The values for $\langle g \rangle$ and $\langle A \rangle$ are given in Table I and compare favorably with those reported by Weissman and Cohn[10] and Weissman and Garner.[11] The two molybdenum isotopes having nuclear spin, Mo^{95} and Mo^{97}, have the same spin ($I = {}^5/_2$) and nearly the same magnetic moment so that it is not possible to resolve the separate hyperfine lines. The C^{13} hyperfine splitting cannot be seen in the spectrum of $W(CN)_8^{3-}$, presumably because the line widths are too large for this species.

Frozen solution spectra of $K_3Mo(CN)_8$ and $K_3W(CN)_8$ were obtained by making up 5×10^{-3} M glycerine solutions and rapidly cooling them by immersion in liquid nitrogen. The esr spectra for these frozen solutions are given in Figures 1 and 2. These spectra can be interpreted in terms of the axial spin Hamiltonian

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta [H_x S_x + H_y S_y] + A I_z S_z + B(I_x S_x + I_y S_y) \qquad (2)$$

using equations first developed by Sands.[13] The spectra in Figures 1 and 2 are characteristic of a frozen liquid spectrum in which $g_\parallel > g_\perp$ and $|B| > |A|$. For both ions the valves of $g_\parallel$ and $g_\perp$ were obtained by analyzing the shape of the center line which arises from those isotopes having zero spin. The value of $|B|$ for $Mo(CN)_8^{3-}$ was obtained by measuring the separation of

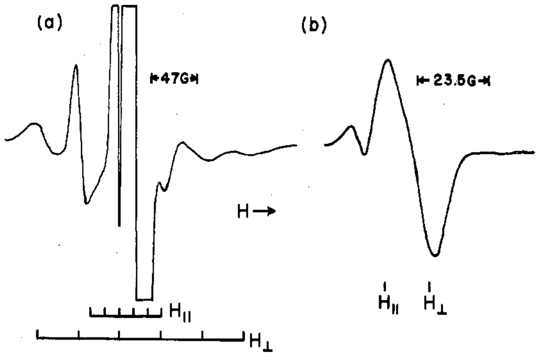

Figure 1.—First derivative of absorption curve for 5×10^{-3} M $K_3Mo(CN)_8$ in glycerine at 77°K: (a) high gain; (b) center peak at low gain.

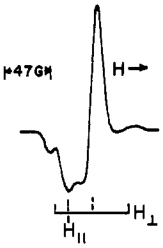

Figure 2.—First derivative of absorption curve for 5×10^{-3} M $K_3W(CN)_8$ in glycerine at 77°K.

the three hyperfine lines on the low-field side of the spectrum from each other and from the $g_\perp$ position of the center line. $|A|$ was estimated by noting that the sharpness and intensity of the $M_I = {}^1/_2$ line could only be explained by assuming that this line is independent of the orientation of the magnetic field and therefore $|A|$ is twice the separation of this line from the $g_\parallel$ position of the center line. For $W(CN)_8^{3-}$ $|B|$ was found by measuring the separation of the two hyperfine lines but it was not possible to measure $|A|$. The C^{13} hyperfine lines could not be detected for either ion in the frozen solution.

The measured values of the spin Hamiltonian parameters are given in Table I. For frozen solution spectra $\langle g \rangle = {}^1/_3(g_\parallel + 2g_\perp)$ and $\langle A \rangle = {}^1/_3(A + 2B)$. The close agreement between the frozen solution and aqueous solution values of $\langle g \rangle$ and $\langle A \rangle$ is strong evidence that the same species is present in both. Further the agreement in the case of $\langle A \rangle$ shows that A and B

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

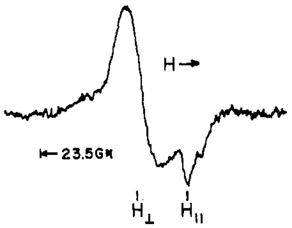

Figure 3.—First derivative of absorption curve for $Mo(CN)_8^{3-}$ in $K_4Mo(CN)_8$ powder.

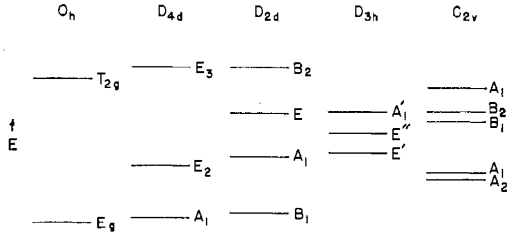

Figure 4.—Energy spacings of d orbitals for five possible arrangements of eight equivalent charges as calculated from crystal field theory. O_h is a cube, D_{4d} is the Archimedean antiprisim, D_{2d} is duodecahedral, D_{3h} is the end-centered trigonal prism, and C_{2v} is a trigonal prism with charges centered in two side faces.

are of the same sign. The value of A listed in parentheses for $W(CN)_8^{3-}$ is calculated assuming $\langle A\rangle$ is the same for both the frozen solution and the aqueous solution.

An attempt was made to observe the ions in a crystal lattice. A solution of $K_4Mo(CN)_8$ containing some $K_3Mo(CN)_8$ was treated with excess methanol to precipitate the $K_4Mo(CN)_8$. A weak spectrum was obtained from the dry powder which is given in Figure 3. It is a characteristic powder spectrum in which $g_\parallel < g_\perp$ and the values are also listed in Table I. The spectrum was too weak and broad to observe any hyperfine lines. A similar experiment was done using the tungsten compounds with similar results. The spectrum was weaker than in the case of molybdenum but values of $g_\parallel$ and $g_\perp$ could be estimated and are given in Table I.

Discussion and Theory

The fact that the resonance is narrow at room temperature indicates that the unpaired electron is in a d orbital which is well separated in energy from the other d orbitals. Since in axial symmetry d_{xz} and d_{yz} are degenerate, the electron must be in a $d_{x^2-y^2}$, d_{xy}, or $d_{3z^2-r^2}$ orbital. Assuming the electron to be in a pure d atomic orbital and using first- and second-order perturbation theory the spin Hamiltonian parameters for a $d_{x^2-y^2}$ ground state are found to be

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

$$g_\perp = 2.0023 - \frac{2\lambda}{E(xz, yz) - E(x^2-y^2)} \tag{3}$$

$$A = P\left[-\kappa - \frac{4}{7} + (g_\parallel - 2.0023) + \frac{3}{7}(g_\perp - 2.0023)\right]$$

$$B = P\left[-\kappa + \frac{2}{7} + \frac{11}{14}(g_\perp - 2.0023)\right]$$

where λ is the spin–orbit coupling parameter, $P = 2.0023 g_N\beta_N\beta\langle r^{-3}\rangle_{av}$, and κ is the isotropic contribution to the hyperfine constant due to polarization of the inner electron spin density by the unpaired d electron. For a d_{xy} ground state eq 3 is also obtained except that $x^2 - y^2$ and xy are interchanged. For a ground state of $d_{3z^2-r^2}$ the results are given by

$$g_\parallel = 2.0023$$

$$g_\perp = 2.0023 - \frac{6\lambda}{E(xz, yz) - E(3z^2 - r^2)} \tag{4}$$

$$A = P\left[-\kappa + \frac{4}{7} - \frac{1}{7}(g_\perp - 2.0023)\right]$$

$$B = P\left[-\kappa - \frac{2}{7} + \frac{15}{14}(g_\perp - 2.0023)\right]$$

The isotropic term κ is normally positive for transition metal ions and has been found to be so for Mo^{5+} in TiO_2[14,15] and $(NH_4)_2InCl_5\cdot H_2O$.[16] Examining eq 3 and 4 we see that $|A| > |B|$ for both d_{xy} and $d_{x^2-y^2}$ ground states and this is found to be the case for Mo^{5+} in TiO_2 and $(NH_4)_2InCl_5\cdot H_2O$ where d_{xy} is the expected ground state. For $d_{3z^2-r^2}$ as the ground state, $|B|$ may be greater than $|A|$. Since $|B| > |A|$ for $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ in glycerine, the ground-state orbital in these ions is the $d_{3z^2-r^2}$ orbital.

Five different structures have been proposed as possible arrangements for eight equivalent ligands about a metal ion. They are: a cube, belonging to symmetry O_h; an Archimedean antiprism, belonging to D_{4d}; duodecahedral, belonging to D_{2d}; a trigonal prism with ligands in the centers of the two end faces, belonging to D_{3h}; and a trigonal prism with ligands centered on two side faces, belonging to C_{2v}. In Figure 4 are shown the spacings of the energy levels for each symmetry as calculated from crystal field theory[17] with the assumption that $\langle r^4\rangle_{av}/a^2\langle r^2\rangle_{av} = 2$ where a is the metal–ligand distance. In O_h the ground state is a degenerate state made up of $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ while in D_{4d} the ground state is the $d_{3z^2-r^2}$ orbital. For D_{2d} the ground state is d_{xy} and for D_{3h} it is a degenerate state made up of d_{xy} and $d_{x^2-y^2}$. For C_{2v} A_2 is the orbital d_{xy} and the lower A_1 is primarily $d_{x^2-y^2}$ while the upper A_1 is primarily $d_{3z^2-r^2}$. Thus the esr results can only be explained by assuming that, in solution, the ion has the Archimedean antiprism configuration, which is the structure found for $Mo(CN)_8^{4-}$ in solution by Stammreich and Sala.[3]

One apparent discrepancy between eq 4 and the experimental spin Hamiltonian is that $g_\parallel$ is less than 2.0023 although not by much in the case of $Mo(CN)_8^{3-}$.

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(14) R. Kyi, *Phys. Rev.*, **128**, 151 (1962).

(15) T. T. Chang, *ibid.*, **A136**, 1413 (1964).

(16) K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 1019 (1965).

(17) See, for example, C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; the calculation for duodecahedral has been reported by M. Randic, *J. Chem. Phys.*, **36**, 2094 (1962), and for the antiprism structure in ref 8.

This is most likely due to the fact that λ is too large to use only second-order perturbation theory. For symmetry D_{4d} it can be shown that

$$g_{\parallel} = 2.0023 \cos 2\alpha + 2k \sin^2 \alpha$$

$$g_{\perp} = 2.0023 \cos^2 \alpha + \sqrt{6}k \sin 2\alpha$$

$$A = P\left[-\kappa + \frac{4}{7} + \frac{8}{7} \sin^2 \alpha - \frac{\sqrt{6}}{7} \sin 2\alpha\right]$$

$$B = P\left[-\kappa - \frac{2}{7} - \frac{4}{7} \sin^2 \alpha + \frac{15}{14} \sqrt{6} \sin 2\alpha\right] \quad (5)$$

$$\tan 2\alpha = -\frac{\sqrt{6}\eta}{1 - \frac{1}{2}\eta}$$

$$\eta = \frac{\lambda}{E(xz, yz) - E(3z^2 - r^2)}$$

$$\sqrt{6}k = (d_1 |l+| d_0)$$

where an attempt to take into account covalent binding is made by allowing k to be less than 1 (its value for a pure d orbital).

Values of P, k, and κP are given in Table II along with values obtained for Mo^{5+} in other environments. For Mo^{5+} in TiO_2 and $(NH_4)_2InCl_5 \cdot H_2O$ eq 3 was used and eq 5 was used for Mo^{5+} in $CaWO_4$ since this appears to be another case where $d_{3z^2-r^2}$ is the ground state. In the calculations it was assumed that A and B were both positive for $Mo^{95,97}$ since g_N is negative for these isotopes. The rather small values of k indicated the inadequacy of trying to represent the effects of covalency by the method employed in eq 5. Since P is proportional to $\langle r^{-3}\rangle_{av}$ the smaller value for $Mo(CN)_8^{3-}$ must mean that the unpaired electron is more delocalized, hence more covalent in bonding orbitals, than it is for Mo^{5+} in TiO_2 and $(NH_4)_2InCl_5 \cdot H_2O$. The small value for $CaWO_4$ is most likely the result of a +5 ion occupying the site of the smaller +6 ion. The smaller magnitude of κP could also mean more delocalization but it could also be due to a small amount of hybridization of 5s with the $4d_{3z^2-r^2}$ orbital since this is allowed in D_{4d} symmetry. Such hybridization makes a negative contribution to κ and hence would reduce the magnitude of κP. Similar comparisons are difficult to make for W^{5+} since less data are available on the esr of W^{5+} compounds. Garifyanov, *et al.*,[18] have reported that $A = 146 \times 10^{-4}$ cm^{-1} for $WO(SCN)_5^{2-}$, and if it assumed that κ is similar to that in Mo^{5+} compounds then $P \sim 90 \times 10^{-4}$ cm^{-1}, which is considerably larger than that found for $W(CN)_8^{3-}$.

TABLE II

VALUES FOR k, P, AND κP FOR Mo^{5+} AND W^{5+}

Ion		k	P(10^{-4} cm^{-1})	κP(10^{-4} cm^{-1})
Mo^{5+} in TiO_2[a]			−44.0	−33.0
Mo^{5+} in $(NH_4)_2InCl_5 \cdot H_2O$[b]			−48.2	−44.0
Mo^{5+} in $CaWO_4$[c]	Mo^{95}	0.32	−26.0	−24.6
	Mo^{97}	0.32	−26.9	−25.4
$Mo(CN)_8^{3-}$		0.08	−24.3	−28.6
$W(CN)_8^{3-}$		0.07	38.5	42.9

[a] See ref 14 and 15. [b] See ref 16. [c] G. H. Azarbayejani and A. L. Merlo, *Phys. Rev.*, **A137**, 489 (1965).

The fact that $g_{\parallel} < g_{\perp}$ for $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ when present in $K_4Mo(CN)_8$ and $K_4W(CN)_8$ suggests that d_{xy} is the ground state. This is consistent with the duodecahedral structure that would be expected in the crystal state since $Mo(CN)_8^{4-}$ in $K_4Mo(CN)_8 \cdot 2H_2O$ possesses this structure.[2] It has been found[19,20] that $g_{\parallel} < g_{\perp}$ for Cr^{5+} in CrO_8^{3-}, which is known to have the duodecahedral structure. The fact that $\langle g \rangle$ for these ions in the duodecahedral configuration is much different from that of the ions in solution is additional evidence that these ions do not possess the duodecahedral configuration in water solution.

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[18] N. S. Garifyanov, B. M. Kozyrev, and V. N. Fedotov, *Dokl. Akad. Nauk SSSR*, **156**, 641 (1964).

[19] B. R. McGarvey, *J. Chem. Phys.*, **37**, 2001 (1962).

[20] J. D. Swalen and J. A. Ibers, *ibid.*, **37**, 17 (1962).

Notes

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Preparations and Properties of Chromium(II) Complexes. IV.[1] Complexes with Acetonitrile and Observations on Tetrahedral Chromium(II)

BY DAVID G. HOLAH AND JOHN P. FACKLER, JR.

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Acetonitrile forms a variety of complexes with halides of first-row transition metals,[2] either by recrystallization of the halide from acetonitrile or by reaction of the metals with halogens (Cl_2, Br_2, I_2) in acetonitrile.[3-6] The majority of the chloride and bromide complexes of Mn(II), Fe(II), Co(II), Ni(II), and Zn(II) are of the type $MX_2 \cdot 2CH_3CN$. Apart from the Co(II) and Zn(II) complexes, they have octahedral structures with (presumably) bridging halides.[3-5] The iodides of Mn(II), Fe(II), Co(II), and Ni(II) form complexes of formula $MI_2 \cdot 3CH_3CN$ which have been shown[3-5] to contain octahedral and tetrahedral metal ions, as in

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[1] Part III: D. G. Holah and J. P. Fackler, Jr., *Inorg. Chem.*, **4**, 1721 (1965).

[2] R. A. Walton, *Quart. Rev.* (London), **19**, 126 (1965).

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[5] B. J. Hathaway and D. G. Holah, *ibid.*, 2408 (1964).

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