$k_{1f} = 120\,M^{-1}\,\text{sec}^{-1}$ and $k_2 = 4.0\,M^{-1}\,\text{sec}^{-1}$. Therefore, for both oxy anions, $K_2^{\text{app}} > K_1^{\text{app}}$ because of differences in the dissociation rate constants; specifically, $k_{-1r} = 0.38\ \text{sec}^{-1}$ *vs.* $k_{-2} = 4 \times 10^{-4}\ \text{sec}^{-1}$ for tungstate. This effect is even larger than that observed for molybdate, where $k_2 \cong 1.8k_{1f}$ and $k_{-1r} \cong 22k_{-2r}$. In both cases, however, the larger dissociation rate constant of the mono relative to the bis complex is due to the presence of the two hydroxo groups in the former and not in the latter compound. The almost certainly present hydroxo groups in the inner coordination shell of the mono complex may donate electrons to the orbitals of the central tungsten(VI) ion by pπ–dπ bonding from ligand donor to metal acceptor.[13] Catechol would not be expected to form π bonds to the metal ion as well as the OH$^-$ group. Therefore, the single catechol molecule in the mono complex is more effectively labilized by the two hydroxyl ions than are either of the bound catechols in the bis complex by one another.

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Registry No. WO_4^{2-}, 14311-52-5; catechol, 321-01-7; 3,4-dihydroxybenzoic acid, 27138-57-4; L-dopa, 59-92-7; pyrogallol, 87-66-1; gallic acid, 149-91-7.

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An Electron Spin Resonance Study of Hexakis(pyridine *N*-oxide)manganese(II) Perchlorate Complexes

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The esr spectra of powdered samples of hexakis(pyridine *N*-oxide)manganese(II) perchlorate complexes doped into the corresponding zinc and cadmium compounds are reported. The pyridine *N*-oxides employed were pyridine, 3-methylpyridine, 4-methylpyridine, 4-nitropyridine, and 4-cyanopyridine *N*-oxides. The analysis of the esr spectra of polycrystalline manganese(II) complexes is discussed. Most of the cadmium complexes exhibit axial symmetry while the ring-substituted zinc complexes generally show rhombic symmetry. The hyperfine coupling constants indicate manganese(II)–pyridine *N*-oxide bonding to be more covalent than manganese(II)–water bonding.

Introduction

Complexes of pyridine *N*-oxide and its derivatives with various metals have been subject of numerous investigations.[1-8] The electronic spectra of cobalt(II) and nickel(II) complexes with 4-substituted pyridine *N*-oxides have been examined both in the solid state and in solution. Values of *Dq* and β, the nephelauxetic parameter, vary from paper to paper since these ligands are labile even in such poor donor solvents as acetonitrile and partial substitution for the pyridine *N*-oxide ligands occurs. Solid-state reflectance and mull (transmission) spectra, however, indicate that pyridine *N*-oxides lie below water in the spectrochemical series for nickel(II) complexes[1] but higher in the series for cobalt(II).[2] Nephelauxetic parameters[1-3] indicate that the metal–ligand covalency in these complexes is dependent on the nature of the substituent group. Generally, the complexes are less covalent than the corresponding aquo compounds. Infrared studies[2,4,5] show substantial reduction of the N–O stretching frequency of the ligand upon complexation. The amount of reduction in the N–O stretch exhibits a marked dependence on both the metal atom and the substituent group on the *N*-oxide ligand. Nmr contact shift work[6] on the Co(II) and Ni(II) complexes of 4-methylpyridine *N*-oxide showed the observed proton shifts to be dominated by a π delocalization mechanism but the importance of the σ delocalization could not be determined due to its slight effect on the proton shift. Appreciable unpaired spin density was observed to exist even on the methyl protons. No crystal structure data are available for the hexakis complexes of pyridine *N*-oxide although the crystal structure of tetrakis(pyridine *N*-oxide)copper(II) perchlorate has been reported.[9] The ligand was shown to be coordinated to the metal *via* the oxygen atom with the pyridine ring bent out of the plane formed by the copper and oxygen atoms. Byers, *et al.*,[4] have noted in the case of the hexakis(pyridine *N*-oxide) complexes that, although the electronic spectra are often interpreted in terms of O_h symmetry, their spectra are among those of few six-coordinate complexes with monodentate ligands which show marked deviation from octahedral symmetry. They[4] pointed out that even the most symmetrical orientations of the ligands will give rise to D_{3d} symmetry while the actual symmetry is probably closer to S_6.

Since very little electron spin resonance (esr) work has been done on complexes of this type and since the magnitude of the zero-field splitting of hexakis complexes of substituted

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pyridine N-oxides with manganese ought to yield information on the degree of distortion of these complexes from true octahedral symmetry, the esr spectra of powder samples of manganese(II) complexes doped into the corresponding zinc and cadmium host lattices were investigated.

Experimental Section

The hexakis complexes of manganese, zinc, and cadmium perchlorates with substituted pyridine N-oxides were prepared according to standard methods described in the literature. Manganese(II)-doped complexes were prepared by dissolving the appropriate metal perchlorate doped with approximately 1% by weight of manganese(II) perchlorate in absolute ethanol and adding the resultant solution to an absolute ethanol solution of the desired pyridine N-oxide. The pyridine N-oxide complex precipitated after stirring. The preparations of the 4-nitro- and 4-cyanopyridine N-oxide complexes involved the use of hot absolute ethanol to solubilize the ligands. The aromatic N-oxides were obtained from Aldrich Chemical Co., Milwaukee, Wis., and the metal perchlorates were purchased from Alfa Inorganics, Beverly, Mass.

Esr spectra were measured with a Magnion Model MVR-12X X-band spectrometer (O. S. Walker Co., Worcester, Mass.) operating at about 9.4 GHz using 6-kHz field modulation and a 12-in. electromagnet. The frequency was monitored with a calibrated absorption wavemeter incorporated in the microwave unit. Field calibration was checked using diphenylpicrylhydrazyl (DPPH) free radical for which $g = 2.0036$. Quartz sample tubes were employed. Reproducibility of spectra from sample to sample and at different levels of Mn(II) doping was excellent.

Theory

Although the esr spectra of polycrystalline samples of copper(II), vanadium(IV), and chromium(III) complexes have been extensively studied in order to investigate their electronic structures, the spectra of powdered Mn(II) compounds of interest to coordination chemists have rarely been investigated. Nevertheless, theoretical treatment of the esr spectra of powdered Mn(II) complexes is straightforward. For the complexes of interest here the spectra could be fit to either an axial or a rhombic spin Hamiltonian. For the axial case (threefold or higher symmetry axis) the spin Hamiltonian for a high-spin ($S = {}^5/_2$) d^5 metal ion, given by Bleaney and Ingram,[10] is

$$\mathcal{H} = g\beta H + D[S_z{}^2 - {}^1/_3S(S+1)] + {}^1/_6a[S_\alpha{}^4 + S_\beta{}^4 + S_\gamma{}^4) - {}^1/_5S(S+1)(3S^2 + 3S - 1)] + {}^1/_{180}F[35S_z{}^4 - 30S(S+1)S_z{}^2 + 25S_z{}^2 - 6S(S+1) + 3S^2(S+1)^2] + AS{\cdot}I \qquad (1)$$

The zero-field terms a, D, and F give rise to the so-called fine lines. For $S = {}^5/_2$ and noting the selection rule $\Delta m_s = \pm 1$, five allowed lines should arise whose field separations are quite dependent on θ, the angle between the applied magnetic field and the symmetry axis. Since g is isotropic, the field direction is taken as the axis of quantization for the electronic Zeeman energy and is independent of the orientation of the crystal with respect to the field. Hence, $g\beta H{\cdot}S$ can be written as $g\beta HS_z$. For the applied field at an arbitrary angle with respect to the symmetry axis, the field separations of the fine lines are then given by

$$\Delta m_s = \pm{}^5/_2 \leftrightarrow \pm{}^3/_2{:}\quad H = H_0 \mp \Bigl[2D(3\cos^2\theta - 1) \pm \frac{32D^2}{H_0}\sin^2\theta\cos^2\theta \mp \frac{D^2}{H_0}\sin^4\theta + \frac{1}{6}F(35\cos^4\theta - 30\cos^2\theta + 3) + 2pa\Bigr] \qquad (2)$$

$$\Delta m_s = \pm{}^3/_2 \leftrightarrow \pm{}^1/_2{:}\quad H = H_0 \mp \Bigl[D(3\cos^2\theta - 1) \mp \frac{4D^2}{H_0}\sin^2\theta\cos^2\theta \pm \frac{5D^2}{4H_0}\sin^4\theta - \frac{5}{24}F(35\cos^4\theta - 30\cos^2\theta + 3) - \frac{5}{2}pa\Bigr] \qquad (3)$$

$$\Delta m_s = +{}^1/_2 \longleftrightarrow -{}^1/_2{:}\quad H = H_0 + \frac{16D^2}{H_0}\sin^2\theta\cos^2\theta - \frac{2D^2}{H_0}\sin^4\theta \qquad (4)$$

where $H_0 = h\nu/g\beta$, $p = 1 - 5\phi$, $\phi = l^2m^2 + m^2n^2 + n^2l^2$; l, m, and n are the direction cosines of H with respect to the cube axes, and θ is the angle between the applied field and the symmetry axis. In a polycrystalline sample the individual crystallites are at random angles to the applied field. This will average to zero any splitting due to the zero-field splitting terms a and F. Since these small quartic zero-field terms will generally contribute splitting on the order of magnitude of the line widths in powder spectra, their contribution can be ignored and only the zero-field term D need be considered. For cases where the complex is very nearly octahedral only the central $\Delta m_s = -{}^1/_2 \leftrightarrow +{}^1/_2$ transition will be observed since it has only a second-order dependence on D. This central fine line will of course be split into a sextet due to electron spin–nuclear spin hyperfine coupling (^{55}Mn, $I = {}^5/_2$). If, however, the zero-field splitting is appreciable, then other electronic transitions will appear in the powder spectrum and the magnitude of the zero-field splitting can be determined. Burns[11] has noted that the powder patterns expected for esr spectra are similar to those for quadrupole powder patterns in nmr spectra, the Hamiltonian being the same if one replaces $3[4I(2I-1)]^{-1}e^2Qq$ by D when the symmetry is axial and η by $3E/D$ when the symmetry is rhombic. These powder patterns for nmr spectra have been determined for a number of spins up to second order by Feld and Lamb[12] for axial symmetry while Strauss[13] has determined the powder patterns in case of lower than axial symmetry. For a powder with randomly oriented crystallites sharp features or lines will only be observed at resonance field values which are stationary with respect to the orientation of the individual crystallite. For the case of an $S = {}^5/_2$, ion, *e.g.*, high-spin Mn(II), in an axially symmetric field esr signals should occur at field positions corresponding to the $\Delta m_s = \pm{}^5/_2 \leftrightarrow \pm{}^3/_2$ and $\pm{}^3/_2 \leftrightarrow \pm{}^1/_2$ transitions for crystallites oriented such that $\theta = 90°$. The $\pm{}^3/_2 \leftrightarrow \pm{}^1/_2$ transitions will have greater intensity than the corresponding $\pm{}^5/_2 \leftrightarrow \pm{}^3/_2$ transitions. The strongest absorption will occur for the central $\Delta m_s = +{}^1/_2 \leftrightarrow -{}^1/_2$ transition whose field position is to a first order independent of orientation. However, as shown by Bleaney and Rubins,[14] this central transition will be split due to second-order terms in D and third-order terms in $AD^2/(g\beta H)^2$. Ignoring the splitting due to the third-order terms in A and D, which will be much smaller than the second-order terms for reasonably large D values, the central transitions will then be split such that resonance lines will be observed for crystallite orientations[14] of $\theta = 90°$ and angles where $\tan^2\theta = 0.8$. Finally, lines will be observed for crystallites at an angle $\theta = 0°$ for the $\Delta m_s = \pm{}^5/_2 \leftrightarrow \pm{}^3/_2$ and $\pm{}^3/_2 \leftrightarrow \pm{}^1/_2$ transitions but these will be much weaker than

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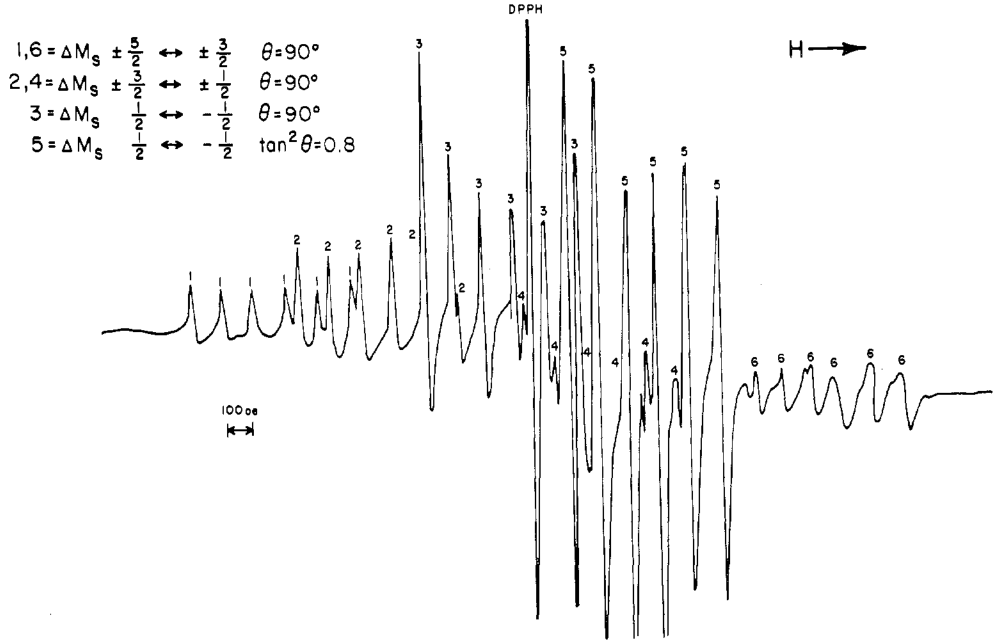

Figure 1. Esr spectrum and assignments for $Mn(N\text{-}pyO)_6(ClO_4)_2$ doped into the corresponding zinc complex.

the $\theta = 90°$ lines and often cannot be observed. Referring to eq 2-4 and letting $\theta = 90°$ it can be seen that the $\Delta m_s = +{}^5/_2 \leftrightarrow +{}^3/_2$ and $-{}^3/_2 \leftrightarrow -{}^5/_2$ transitions will be separated by $4D$ and the $+{}^3/_2 \leftrightarrow +{}^1/_2$ and $-{}^3/_2 \leftrightarrow -{}^1/_2$ transitions by $2D$, and the separation between the two central $(+{}^1/_2 \leftrightarrow -{}^1/_2)$ transitions is given by $5.6D^2/H_0$ with all parameters expressed in gauss. The outermost fine lines on each side of the central fine lines are then due to the $\Delta m_s = \pm{}^5/_2 \leftrightarrow \pm{}^3/_2$ transitions at $\theta = 90°$. The next sets of fine lines on the high- and low-field side of DPPH can generally be assigned to the $\Delta m_s = \pm{}^3/_2 \leftrightarrow \pm{}^1/_2$ transitions at $\theta = 90°$. However, if the second-order terms in D are large enough, the central transition at an orientation such that $\tan^2\theta = 0.8$ can be displaced outside of the $\pm{}^3/_2 \leftrightarrow \pm{}^1/_2$ transitions. The low-field central transition can be assigned to the $\Delta m_s = +{}^1/_2 \leftrightarrow -{}^1/_2$ transition at $\theta = 90°$ and the high-field transition to the $\Delta m_s = +{}^1/_2 \leftrightarrow -{}^1/_2$ transition at an orientation $\tan^2\theta = 0.8$. Determination of the D value allows for the evaluation of H_0 from which g can be determined by comparing the resonant field value (H_0) of the complex to that of DPPH free radical and utilization of the expression

$$g = g_s(h\nu/\beta)/[g_s(\delta H) + (h\nu/\beta)] \tag{5}$$

where g_s is the g value of DPPH (2.0036), δH, the field separation (negative for a low-field displacement), and, ν, the klystron frequency. The electron spin-nuclear spin hyperfine coupling constant, A, can be determined[10] by taking the average of all the hyperfine line separations. Thus, three separate methods of obtaining D are available and an accurate value of the zero-field splitting parameter can be determined. Figure 1 shows the esr spectrum of polycrystalline $Mn(N\text{-}pyO)_6(ClO_4)_2$ doped into the corresponding zinc host lattice and assignments of the various lines to their electronic transitions.

When the complex has less than axial symmetry, the powder spectrum is not so simple. In rhombic symmetry the x and y axes are no longer equivalent and, ignoring zero-field terms quadratic in spin, the spin Hamiltonian is

$$\mathcal{H} = g\beta HS + D(S_z^2 - {}^1/_3 S(S+1)) + E(S_x^2 - S_y^2) + ASI \tag{6}$$

For an applied field directed at an arbitrary angle to the z axis the field positions of the transitions are given by[15]

$$\begin{aligned} H = {} & H_0 - (m_s - {}^1/_2)[D(3(\cos\theta)^2 - 1) - 3E\cos \\ & 2\phi((\cos\theta)^2 - 1)] + \{[4S(S+1) - 24m_s(m_s - 1) - \\ & 9]/2H_0\}[(D - E\cos 2\phi)^2(\sin\theta\cos\theta)^2 + (E\sin \\ & 2\phi)^2(\sin\theta)^2] - \{[2S(S+1) - 6m_s(m_s - 1) - \\ & 3]/8H_0\}[D(\sin\theta)^2 + E\cos 2\phi(1 + (\cos\theta\sin 2\phi)^2] \end{aligned} \tag{7}$$

where θ is the angle between H and the z axis and ϕ is the angle between the projection of H in the xy plane and the x axis. The term $E\cos 2\phi$ in the last line of eq 7 is incorrectly given as $E\cos^2\phi$ in ref 15. As for axial symmetry, sharp lines are observed in the esr powder spectrum at resonant fields corresponding to only certain orientations of the crystallites with respect to the applied field. Thus, lines will be observed[15] for the $\Delta m_s = \pm{}^5/_2 \leftrightarrow \pm{}^3/_2$ and $\pm{}^3/_2 \leftrightarrow \pm{}^1/_2$ transitions when the field is along the x, y, or z magnetic axes. Referring to eq 7, it can be seen that for H parallel to z the $+{}^5/_2 \leftrightarrow +{}^3/_2$ and $-{}^5/_2 \leftrightarrow -{}^3/_2$ transitions will be separated by $8D$ and the $+{}^3/_2 \leftrightarrow +{}^1/_2$ and $-{}^3/_2 \leftrightarrow -{}^1/_2$ transitions by $4D$. For most values of D and E the $\pm{}^5/_2 \leftrightarrow \pm{}^3/_2$ transitions with H parallel to z will be the outermost lines observed on each side of H_0. However, they will not be symmetrically displaced about H_0 due to second-order terms in E. When H is parallel to the y axis, the separation between the $+{}^5/_2 \leftrightarrow +{}^3/_2$ and $-{}^3/_2 \leftrightarrow -{}^5/_2$ transitions is given by $4D + 12E$ and that between the $+{}^3/_2 \leftrightarrow +{}^1/_2$ and $-{}^1/_2 \leftrightarrow -{}^3/_2$ transitions by $2D + 6E$. The y transitions can often nearly overlap with the z transitions depending on the size of E. In general, the $\pm{}^5/_2 \leftrightarrow \pm{}^3/_2$ transitions for $H \| y$ will be the second outermost lines observed on the high- and low-field sides of H_0. When the field is directed along the x axis, the separation between the $+{}^5/_2 \leftrightarrow +{}^3/_2$ and $-{}^3/_2 \leftrightarrow -{}^5/_2$ transitions is given by $4D - 12E$ and that between the $+{}^3/_2 \leftrightarrow +{}^1/_2$ and $-{}^3/_2 \leftrightarrow -{}^1/_2$ transitions by $2D - 6E$. Unfortunately, the x transitions are often buried under the strong central transitions and cannot be observed. As E approaches zero, the various field separations approach those observed in the axial case and for very small rhombic distor-

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Table I. Spin-Hamiltonian Parameters

Host metal ion	Ligand	g (±0.002)	$-A$ G	$-A$ $\times 10^4$ cm^{-1}	D G	D $\times 10^4$ cm^{-1}	E G	E $\times 10^4$ cm^{-1}
Zn	Pyridine *N*-oxide	1.998	94	88	445	415	0	0
Cd	Pyridine *N*-oxide	2.003	94	88	461	431	0	0
Zn	3-Methylpyridine *N*-oxide	1.996	92	86	730	680	91	85
Cd	3-Methylpyridine *N*-oxide	2.003	92	86	520	482	0	0
Zn	4-Methylpyridine *N*-oxide	2.000	95	89	770	719	145	135
Cd	4-Methylpyridine *N*-oxide	2.003	95	89	680	642	0	0
Zn	4-Nitropyridine *N*-oxide	1.996	90	83	515	478	160	149
Cd	4-Nitropyridine *N*-oxide	2.001	90	83	491	458	102	95
Zn	4-Cyanopyridine *N*-oxide	2.001	90	83	189	177	0	0
Cd	4-Cyanopyridine *N*-oxide	2.006	90	83	224	209	<40	

tions E cannot be determined. In rhombic symmetry the splitting of the strong central transitions is a function of the magnitude of E relative to D, *i.e.*, the extent of rhombic distortion. Strauss[13] has determined the separation of these central lines for various values of the E/D ratio. Since his calculations[13] were performed for nuclear quadrupole powder patterns in nmr, application to esr requires replacing η by $3E/D$. For E/D equal to $^1/_3$, for instance, the central $+^1/_2 \leftrightarrow -^1/_2$ transition will split into four lines (each line of course will be split into six hyperfine components) with field positions $H_0 + 16D^2/3H_0, H_0, H_0 - 2D^2/3H_0$, and $H_0 - 8D^2/3H_0$. Hence, the values of D, E, and H_0 can be determined from the outer transitions and the positions of the central lines calculated and compared to experimental data to check accuracy. The g and A values can be determined by the method employed for axial symmetry. Figure 2 gives the esr spectrum and assignments for Mn(4-Me-N-pyO)$_6$(ClO$_4$)$_2$ doped into the corresponding zinc complex.

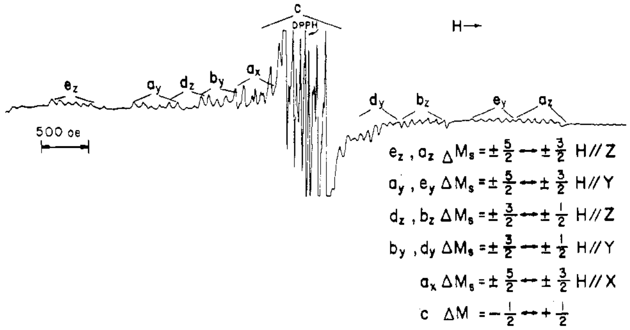

Figure 2. Esr spectrum and assignments for Mn(4-Me-N-pyO)$_6$(ClO$_4$)$_2$ doped into the corresponding zinc complex.

Results and Discussion

Table I collects the spin-Hamiltonian parameters for various pyridine N-oxide complexes of manganese(II) doped into the corresponding zinc and cadmium host lattices. Most of the cadmium complexes exhibit axial symmetry while the ring-substituted zinc complexes generally show rhombic symmetry. The magnitudes of the zero-field splitting show that *all* of the complexes are markedly distorted from octahedral symmetry. Byers, *et al.*,[4] have noted that the effective symmetry of a complex is dependent on the electronic symmetry, governed by metal ion–ligand wave function interaction, as well as the geometry of the surrounding ligands. Hexakis(pyridine N-oxide) complexes of Co(II) and Ni(II) show marked deviation in their electronic and infrared spectra from octahedral symmetry unlike those of most six-coordinate complexes with monodentate ligands. The zero-field splitting in the complexes studied here also shows a dependence on the substituent group on the pyridine ring and the host lattice.

Title[16] first noted the effect of variation of the host metal ion on zero-field splitting parameters. He studied a series of group II–IV compounds, such as ZnS, doped with Mn(II) and found for these cubically symmetric systems that the a value decreased as the ionic radius of the host metal increased. Since Walsh[17] and Feher[18] found that uniaxial pressure on Mn(II)-doped single crystals produced increased zero-field splitting, Title[16] also concluded that substitution of an Mn(II) ion for a smaller host ion would be equivalent to exerting uniaxial pressure and hence produce similar effects. The theoretical work of Watanabe[19] and Powell, *et al.*,[20] using point charge models found a to be dependent on the strength of the cubic crystalline field and D dependent on the axial crystalline field. Presumably, substitution of Mn(II) for a smaller ion would increase the strength of the surrounding field while the opposite would be true for a larger ion. This would produce the same effect noted by Title.[16] Partial verification of this interpretation was given by the results of Hall, *et al.*,[21] who calculated a for Mn(II) doped into KMgF$_3$ using Powell's approach. The calculated value of a was smaller than the experimental value. Since Dq values employed in the calculation were those for KMnF$_3$, the calculated a value would be smaller than experimental where Dq should be that for Mn(II) in the KMgF$_3$ lattice. However, covalency effects were also likely to produce some variation between experimental and calculated values. Sharma, *et al.*,[22] modified their theoretical calculations of zero-field splittings to include covalency effects and found overlap contributions to the D and E values to be of considerable importance. Furthermore, these contributions were found to be opposite in sign to the contribution of the point charge crystalline field for MnF$_2$. Woltermann[23] attributed variation of D values for Mn(II) doped into an isomorphic series of antipyrine complexes to the degree of distortion from octahedral symmetry for each host lattice. Hence, less distortion would be expected for a lead(II) ion than for a small magnesium(II) ion. The values determined for the pyridine N-oxide complexes are in qualitative agreement with this interpretation. Reference to Table I shows this trend to be generally followed for pyridine N-oxide complexes. However, a number of notable discrepancies exist.

For the pyridine N-oxide and 4-cyanopyridine N-oxide complexes the D value is slightly larger for the cadmium host lattice. Since the difference in the size (the ionic radii for Mn(II), Zn(II), and Cd(II) are 0.80, 0.69, and 0.92 Å,

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respectively) of zinc and cadmium ions is pronounced, this result is unexpected. For the other complexes the expected zero-field splitting in the zinc host lattice is observed. It can be expected that upon substitution of a methyl or other group for one of the ring hydrogens steric crowding of the six ligands about the metal ion would be increased, hence, producing greater distortion from octahedral symmetry. While both the 3- and 4-methyl-substituted pyridine *N*-oxide complexes exhibit enhanced zero-field splitting, the zero-field splitting is less for the 4-nitro- and 4-cyanopyridine *N*-oxide complexes. Steric considerations obviously will not account totally for the magnitudes of D and E in these complexes. Indeed, there is no reason from steric considerations alone why the zero-field splitting should be larger for the 4-methylpyridine *N*-oxide complex than for the 3-methyl-substituted complex. In fact, if free rotation of the pyridine ring about the bent N–O bond occurs, steric hindrance and, hence, distortion would be expected to be larger for the 3-picoline *N*-oxide complexes. The zero-field splitting, however, does not reflect this.

Apparently, covalency effects are also involved. Herlocker, *et al.*,[1] noted that the N–O stretching frequency was higher the greater the electron-withdrawing ability of the substituent group. Furthermore, upon complexation to a metal ion the largest shifts in the N–O frequencies were observed for the ligands which had strong electron-withdrawing substituents on them. Ability of the withdrawing group to enhance metal–ligand back-bonding was given as the primary reason for these observations. Such back-bonding was seen to be especially important for the nitro-substituted complex with nickel. Back-bonding was also invoked to account for the amomalously high Dq value observed for the 4-nitropyridine *N*-oxide complex with nickel. Although the 4-cyano-substituted complexes have not been extensively investigated, infrared data for the free ligand and hexakis iron(III) complex[24] indicate the cyanide group is a more effective withdrawing group than the nitro group, exhibiting a higher N–O stretch for the ligand and a larger N–O frequency shift for the complex. Presumably, back-bonding is also quite important for this ligand. The electron-withdrawing nature of the substituent group on the pyridine ring could act in an opposite manner on the zero-field splitting than steric distortion. Hence, for the nitro-substituted complex zero-field splitting is smaller than for either of the methyl-substituted ligands, even though steric considerations would predict the opposite to be true. The cyano complexes exhibit even smaller zero-field splitting. The 4-methyl-substituted complex exhibits larger zero-field splitting than its 3-substituted analog. Jaffe[25] has noted that a methyl group substituted in the 4 position behaves as an electron-donating group while a methyl group in the 3 position acts as a withdrawing group. Since sterically the effect of the methyl groups can be expected to be about the same, the difference in zero-field splitting must be attributed to the difference in withdrawing ability. Since detailed crystallographic data are lacking for these complexes, the magnitude and sign of the various contributions to D and E cannot be known and the above arguments are not unambiguous; *e.g.*, more effective crystal packing for the 4-cyano complex cannot be ruled out. The present data do indicate, however, that the electron-withdrawing power of the substituent group is of importance to the magnitude of the zero-field splitting and that the relative degree of structural distortion cannot be deduced from the magnitude of the zero-field splitting.

The g values in Table I are consistent with those expected for an ion with an S ground state; *i.e.*, the g values are close to that of the free electron, 2.0023, due to very small orbital contributions to the ground state. Due to almost negligible orbital contribution the effect of change of host metal ion on the g value is also very small. For the pyridine *N*-oxide complexes a small positive g shift is observed on going from the zinc to the cadmium host lattice. This is in line with the observations of Title[16] in his study of Mn(II)-doped group II–IV compounds.

The electron spin–nuclear spin hyperfine coupling constants, A, in Table I show that there is little metal–ligand covalency. Watson and Freeman[26] have demonstrated that core polarization by the unpaired d electrons of Mn on Mn 3s orbitals is mainly responsible for the A value. Any transfer of unpaired spin density either metal to ligand or *vice versa* would be expected to decrease the magnitude of A. Van Wieringen[27] noted a steady decrease of A with increasing metal–ligand covalency. Title[16] and Matamura[28] have found A to be linearly related to the Pauling ionicities of the Mn(II) complexes. The A values of pyridine *N*-oxides indicate that these ligands are somewhat more covalent than water. Whyman, *et al.*,[2] and Herlocker, *et al.*,[1] however, have found the pyridine *N*-oxide ligands generally to be less covalent, as indicated by nephelauxetic parameters, than water in their Co(II) and Ni(II) complexes. Nephelauxetic parameters for the Ni(II) complexes increase[1] with increasing electron-withdrawing ability of the substituent. The A values in Table I also exhibit this trend. In any event the pyridine *N*-oxide complexes exhibit only relatively small covalency as is usual[16,23,27,29] for manganese complexes with oxygen-donor ligands.

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Registry No. Zn(*N*-pyO)$_6$(ClO$_4$)$_2$, 23195-17-7; Cd(*N*-pyO)$_6$(ClO$_4$)$_2$, 23105-02-4; Zn(3-Me-*N*-pyO)$_6$(ClO$_4$)$_2$, 40895-25-8; Cd(3-Me-*N*-pyO)$_6$(ClO$_4$)$_2$, 40895-26-9; Zn(4-Me-*N*-pyO)$_6$(ClO$_4$)$_2$, 24470-65-3; Cd(4-Me-*N*-pyO)$_6$(ClO$_4$)$_2$, 40895-33-8; Zn(4-NO$_2$-*N*-pyO)$_6$(ClO$_4$)$_2$, 24470-68-6; Cd(4-NO$_2$-*N*-pyO)$_6$(ClO$_4$)$_2$, 41004-12-0; Zn(4-CN-*N*-pyO)$_6$(ClO$_4$)$_2$, 40895-31-6; Cd(4-CN-*N*-pyO)$_6$(ClO$_4$)$_2$, 41004-11-9; Mn(*N*-pyO)$_6$(ClO$_4$)$_2$, 23608-36-8; Mn(3-Me-*N*-pyO)$_6$(ClO$_4$)$_2$, 22386-19-2; Mn(4-Me-*N*-pyO)$_6$(ClO$_4$)$_2$, 21460-60-6; Mn(4-NO$_2$-*N*-pyO)$_6$(ClO$_4$)$_2$, 21460-59-3; Mn(4-CN-*N*-pyO)$_6$(ClO$_4$)$_2$, 40895-27-0.

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