as was the case in these experiments, it is likely that the second coordination site of mercury(II) is occupied by OH^-.[2] Substitution occurs rapidly at mercury(II), so this can be displaced rapidly by better ligands, *e.g.*, mercaptides, chloride, etc.

It may be concluded that the reaction at 25° between Urd and Hg(II) or CH_3Hg^{II} in aqueous perchlorate solution at pH 7–9 involves displacement of the proton from N(3) and coordination of mercury. The solution Raman spectra are not at all consistent either with coordination to a neutral carbonyl oxygen or with an electrophilic attack at carbon. At high hydrogen ion concentrations or in the presence of a good ligand for mercury, *e.g.*, chloride ion, substitution of the ring proton is blocked and weak binding to a carbonyl oxygen can occur. The CH_3Hg^{II} ion apparently is not a sufficiently strong electrophile to displace H(5) and form the mercuri nucleotide at pH 8.

Registry No. $HgCl_2 \cdot 2Ura$, 53293-38-2; 5-Hg-UTP, 53293-39-3.

References and Notes

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Electron Paramagnetic Resonance Investigation of Crystal Field, Nuclear Quadrupole, and Structural Properties of Two Manganese(II) Compounds

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The electron spin resonance spectra of *trans*-$[Mn(acac)_2(H_2O)_2]$ doped into a diamagnetic, isomorphous host are reported. The unit cell parameters of another diamagnetic lattice, $[Zn(C_5H_5NO)_6](ClO_4)_2$, are reported ($C_5H_5NO$ is pyridine *N*-oxide), and the electron spin resonance spectra of $[Mn(C_5H_5NO)_6](ClO_4)_2$ in this host are reported. The principal features of interest are the large zero-field splittings in both compounds and a rhombic term in the acetylacetonate compound. The crystal field parameters are $D = 702$ G and $E = 205$ G in the acetylacetonate and $D = 410$ G for the C_5H_5NO compound. Also reported is the observation of $\Delta m = \pm 1$ lines, which are split by a nuclear electric quadrupole term, Q'. The parameters g, A, and B are also reported.

Introduction

Among the paramagnetic salts of the iron group, those of Fe(III) and Mn(II) are of special interest, for these ions behave as nearly ideal paramagnets.[1] The ^6S ground state is well isolated from the excited (optical) states, which causes many salts to exhibit a simple Curie behavior to low temperatures and also to have electronic relaxation times long enough such that many compounds exhibit electron spin resonance absorption at ambient temperatures. As a result, the epr spectrum of manganese(II) in particular has been reported in many host compounds, most of them being either hydrates or simple ionic salts.[2] Only a few chelate compounds[3] have been investigated, and so we report here an epr investigation of the divalent manganese chelate *trans*-diaquobis(acetylacetonato)manganese(II), *trans*-$[Mn(acac)_2(H_2O)_2]$. Also chosen for study was a divalent manganese salt hexakis(pyridine *N*-oxide)manganese(II) perchlorate, $[Mn(C_5H_5NO)_6](ClO_4)_2$.

The spectra are analyzed in terms of a spin Hamiltonian and the necessary parameters obtained. Of special significance, the use of single crystals and the large deviations from cubic symmetry have permitted the investigation of the nuclear electric quadrupole contribution to the splitting of nuclear forbidden transitions; the quadrupole terms are of current concern in discussions of chemical bonding.[4]

Experimental Section

trans-$[Mn(acac)_2(H_2O)_2]$ and the diamagnetic host compound *trans*-$[Mg(acac)_2(H_2O)_2]$ were prepared in a similar fashion. A stoichiometric amount of acetylacetone in methanol was added to an aqueous solution of $MnCl_2 \cdot 4H_2O$ and the mixture was made basic with sodium acetate.[5] After heating, the mixture was placed in the refrigerator for several hours. The light yellow precipitate was filtered under nitrogen and dried in a desiccator. The Mg(II) compound is white and it may also be prepared by making the acetylacetone–$MgCl_2 \cdot 6H_2O$ mixture basic with ammonium hydroxide. The Mn(II) compound is light sensitive and decomposes on prolonged exposure to the air, so it was kept under nitrogen and in the dark.

Single crystals of 0.5% $Mg(Mn^{II})(acac)_2(H_2O)_2$ were grown from dimethylformamide solution. The doped compound was prepared by allowing the $MgCl_2 \cdot 6H_2O$ to react with acetylacetone in the presence of 0.5% $MnCl_2 \cdot 4H_2O$. The crystals were grown by evaporating DMF under nitrogen and in the dark.

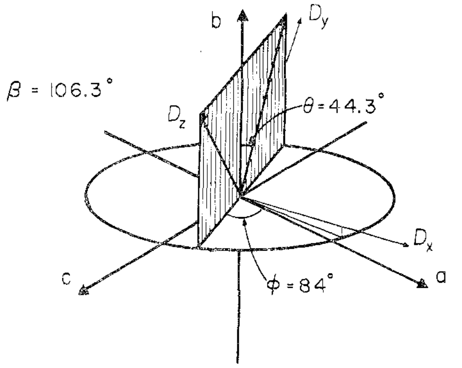

Figure 1. The orientation of the crystal field axes of one molecule of *trans*-[$Mn(acac)_2(H_2O)_2$] with respect to the crystallographic axes is shown. The shaded plane contains the D_z axes of both molecules as well as the crystal *b* axis.

Hexakis(pyridine *N*-oxide)manganese(II) perchlorate and the diamagnetic host compound [$Zn(C_5H_5NO)_6$](ClO_4)$_2$ were prepared by mixing together stoichiometric methanolic solutions of the hydrated metal perchlorate and purified pyridine *N*-oxide.[6] The pyridine *N*-oxide was obtained from Aldrich and purified by vacuum sublimation. The manganese compound is heat, air, and light sensitive so it was stored in a refrigerator in the dark under nitrogen.

Single crystals of [$Zn(Mn^{II})(C_5H_5NO)_6$](ClO_4)$_2$ doped at 0.5% were prepared by mixing the metal perchlorates and then causing them to react with pyridine *N*-oxide. The doped compound was dissolved in DMF and the solution was evaporated in the dark under nitrogen.

The crystal structures of a series of *trans*-[$M(acac)_2(H_2O)_2$] compounds, M = Mg,[7] Mn,[8] Co,[9] Ni,[10] have been reported, all the compounds being isomorphous. They are monoclinic, space group $P2_1/c$, with two centrosymmetric molecules in the unit cell. The metal atom is at the center of symmetry and is surrounded by four oxygen atoms of the acetylacetonate and two axial water molecules, forming a tetragonally distorted octahedron. The crystals exhibit pronounced pleochroism, which is greatest when plane-polarized light is traveling perpendicular to (001). The pleochroism is least when light is perpendicular to (100). The molecular axes are related to the crystallographic axes as shown in Figure 1.

There appears to have been no crystal structure determination described in the literature for hexakis(pyridine *N*-oxide)metal perchlorates of the first transition series. Single crystals of the Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} compounds have been grown and all have the same morphological structure and appear to be isomorphous. A preliminary X-ray study of the zinc compound was therefore undertaken to determine some of the symmetry properties of the crystal lattice.

Zero-level precession photographs were taken on three crystallographic axes and determined the lattice as rhombohedral. The space group was determined as either $R3$ or $R\bar{3}$, differing only by a center of symmetry. The unit cell parameters are $a = 9.607$ Å and $\alpha = 81°20'$. The calculated density with one molecule per unit cell is 1.53 g/cm^3; the measured density by the flotation technique is 1.57 g/cm^3.

The rhombohedral space group with but one molecule in the unit cell suggests a structure with the coordination polyhedron of pyridine *N*-oxides trigonally distorted about the central metal and the two perchlorate anions above and below on the C_3 axis. No refinement was done on intensity data to determine the structure uniquely, but the one suggested here is consistent with the data obtained from the precession photographs and, as will be shown, from the epr studies.

The spectra were taken on a JEOLCO-3BS epr instrument operating at both X- and Q-band frequencies (9.4550 and 35.089 GHz, respectively). The spectra were taken at both ambient and liquid nitrogen temperatures. Both compounds were mounted using the precession camera for alignment on the proper axis or plane and a transfer goniometer adapted for mounting on the epr X-band cavity.

Theoretical Background

The epr spectrum of the manganese ion may be analyzed in terms of a spin Hamiltonian with parameters reflecting the symmetry of the crystalline field. In this report we have crystal field environments of trigonal, [$Mn(C_5H_5NO)$](ClO_4)$_2$, and rhombic, $Mn(acac)_2(H_2O)_2$, symmetry. Neglecting nuclear interaction, the electronic spin Hamiltonian can be written[11] in a form convenient for analysis as

$$\begin{aligned}\mathcal{H}_E = {} & \beta(\mathbf{H}\cdot g\cdot \mathbf{S}) + D[S_z^2 - {}^1/_3 S(S+1)] + {}^1/_6 a[S_\xi^4 + S_\eta^4 + \\ & S_\zeta^4 - {}^1/_5 S(S+1)(3S^2 + 3S - 1)] + 180F[35S_z^4 - \\ & 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + \\ & 3S^2(S+1)^2] + E(S_y^2 - S_x^2)\end{aligned} \qquad (1)$$

where the ξ, η, ζ coordinate system is due to the cubic field. The *z* axis of the acetylacetonate molecule (tetragonal) may be assumed to coincide with the ξ axis of the cubic field, but the *z* axis of the pyridine *N*-oxide complex is along the [111] axis of the ξ, η, ζ system. The quantity *a* is the magnitude of the cubic field, *D* and *E* are the quadrupolar components of the crystal field, and *F* is the fourth-order crystal field spin term.

For the axial case ($E = 0$), the energy levels for the allowed electronic transitions can be evaluated using perturbation theory and they are given by the expressions[12]

$$\Delta M = \pm {}^5/_2 \longleftrightarrow \pm {}^3/_2$$

$$\begin{aligned}g\beta H = {} & g\beta H_0 \mp [2D(3\cos^2\theta - 1) + 2pa + {}^1/_6 Fq] - \\ & 32\delta_1 + 4\delta_2 + \epsilon_1\end{aligned} \qquad (2a)$$

$$\Delta M = \pm {}^3/_2 \longleftrightarrow \pm {}^1/_2$$

$$\begin{aligned}g\beta H = {} & g\beta H_0 \mp [D(3\cos^2\theta - 1) - {}^5/_2 pa - {}^5/_{24} Fq] + \\ & 4\delta_1 - 5\delta_2 + \epsilon_2\end{aligned} \qquad (2b)$$

$$\Delta M = {}^1/_2 \longleftrightarrow -{}^1/_2$$

$$g\beta H = g\beta H_0 + 16\delta_1 - 8\delta_2 + \epsilon_3 \qquad (2c)$$

where H is the field at which a transition occurs with the application of a frequency ν and $H_0 = h\nu/g\beta$ is the field at which a transition would occur if all fine-structure terms had been zero.

The term p is given[13] by $1 - 5\phi$ with $\phi = (\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2)$ where α_1, α_2, α_3 are the direction cosines of H referred to the axes of the cubic field. The term q is a function of θ: $q = 35\cos^4\theta - 30\cos^2\theta + 3$. Along the principal magnetic axes, the parallel and perpendicular directions, the a and F terms have the same coefficient; therefore no attempt was made to separate the parameters.

Second-order axial terms are included in δ_1 and δ_2 where

$$\delta_1 = \frac{D^2}{g\beta H_0}\cos^2\theta\sin^2\theta$$

$$\delta_2 = \frac{D^2}{4g\beta H_0}\sin^4\theta$$

The second-order terms due to the cubic field are

$$\epsilon_1 = \frac{a^2}{g\beta H_0}\left[\frac{5}{3}\phi(1 - 7\phi)\right]$$

$$\epsilon_2 = \frac{-a^2}{g\beta H_0}\left[\frac{5}{48}(3 + 178\phi - 625\phi^2\right]$$

$$\epsilon_3 = \frac{a^2}{g\beta H_0}\left[\frac{10}{3}\phi(7 - 25\phi)\right]$$

A satisfactory interpretation of the spectra of the pyridine *N*-oxide complex did not require the addition of a rhombic term to the spin Hamiltonian so that $E = 0$.

For the rhombic case of $Mn(acac)_2(H_2O)_2$, there is no simple formula that gives the energy eigenvalues of the fine-structure terms as a function of orientation. Therefore the epr parameters were fitted by computer diagonalization of the spin Hamiltonian for the three directions with the field parallel to each of the crystal field axes. This was accomplished using the cyclic permutation of coordinates, the high-field approximation, and then a least-squares fit of the eigenvalues of the spin Hamiltonian to the observed fine-structure resonance fields. The fitting program was carried out over all three orientations simultaneously.

Thus far we have only considered the fine-structure terms in the analyses. The effects of the nuclear spins of manganese ($I = {}^5/_2$) can be expressed by adding to eq 1 nuclear hyperfine structure, nuclear Zeeman and nuclear electric quadrupole moment terms, respectively

$$\mathcal{H}_N = \mathbf{S}\cdot A\cdot\mathbf{I} + \beta_n\mathbf{H}\cdot g_I\cdot\mathbf{I} + \mathbf{I}\cdot P\cdot\mathbf{I} \qquad (3)$$

The complete spin Hamiltonian of a manganese(II) ion is then

$$\mathcal{H} = \mathcal{H}_E + \mathcal{H}_N$$

Forbidden ($\Delta m = \pm 1$) nuclear hyperfine lines in the spectra of manganese ions were first observed by Bleaney and Ingram.[1] These lines appeared as weak-intensity doublets between the main allowed hyperfine lines. Bleaney and Rubins[14] observed the $\Delta m = \pm 2$ transitions in addition to the $\Delta m = \pm 1$ and developed a theory for the angular dependence of the intensity of these lines. The lines arise from an admixture of spin states due to off-diagonal terms in the spin Hamiltonian when the magnetic field is not directed along a principal magnetic axis or more specifically a proper rotational axis of the D tensor. The separation of these doublets is due in part to the presence of nuclear magnetic hyperfine structure interaction and nuclear electric quadrupole terms in the spin Hamiltonian. Bleaney and Rubins calculated the doublet separation to second order in A. Third-order terms were calculated by numerous authors.[15-21] These equations are for small separations from the magnetic z axis. These equations are suitable for the trigonal pyridine N-oxide symmetry but for our calculations on $Mn(acac)_2(H_2O)_2$ we found it necessary to add an angular term since the analysis is more feasible when the crystal is oriented near the D_x axis. Also we must add a term which reflects a quadrupolar dependence on the rhombic field and possible quadrupolar anisotropy. For this reason the angular and rhombic terms described by Folen[22] are used. For the nuclear "forbidden" transitions, the doublet separation (where $k = 0, \pm 1, \pm 2$)

$$\delta H_d = H(|{}^1/_2, k + {}^1/_2\rangle \rightarrow |{}^1/_2, k - {}^1/_2\rangle) - H(|{}^1/_2, k - {}^1/_2\rangle \rightarrow |{}^1/_2, k + {}^1/_2\rangle)$$

is given by the relation

$$\delta H_d = \frac{17A^2}{2H} + 2\frac{g_N\beta_N}{g\beta}H - \left[\left(Q' - \frac{4A^2D}{H^2}\right)(3\cos^2\theta - 1) + 3\left(Q'' - 4\frac{A^2E}{H^2}\right)\sin^2\theta\cos 2\phi + 25\frac{A^3}{2H^2}\right](2k) \qquad (4)$$

where the parameters are expressed in gauss and $k \pm {}^1/_2$ represents the nuclear spin states. The angles θ and ϕ are the angles the magnetic field makes with the z and x crystal field axes, respectively.

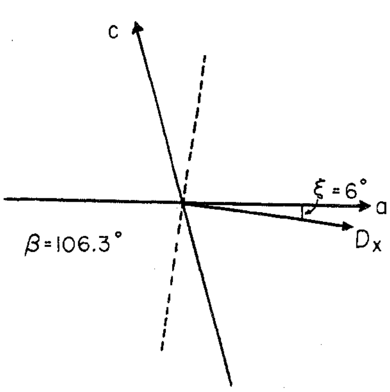

Figure 2. The orientation of the crystal in the (010) plane for spectrum of D_x axes. The D_x vector of one molecule is 6° above the plane; the D_x axis of the other is 6° below the plane. Both molecules are magnetically equivalent because of the twofold screw axis. The magnetic field direction is the projection of the D_x vectors on the (010) plane.

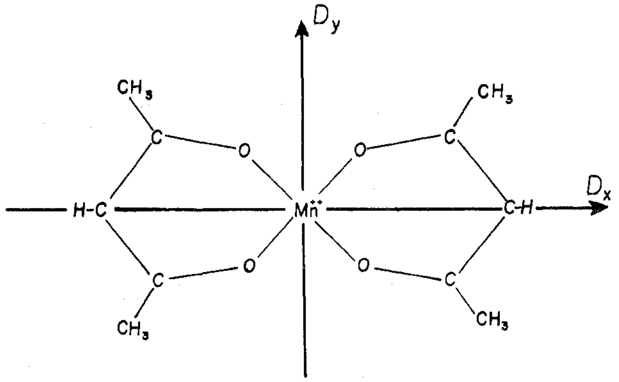

Figure 3. The orientation of the D tensor with respect to molecular coordinates. The D_z vector comes up out of the paper.

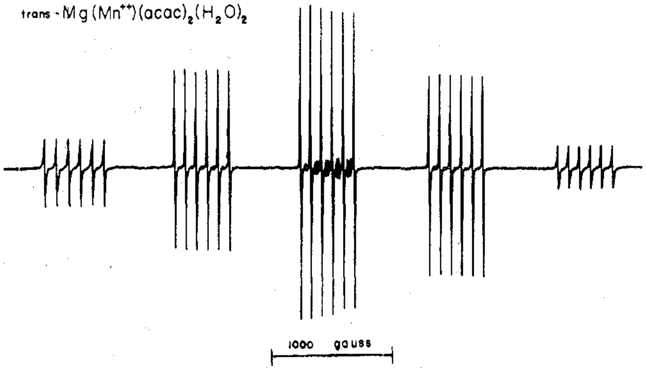

Figure 4. Q-Band liquid nitrogen epr spectrum of *trans*-[$Mg(Mn^{II})(acac)_2(H_2O)_2$] oriented as shown in Figure 2.

Results

The [$Mg(Mn^{II})(acac)_2(H_2O)_2$] crystal was first mounted with $H \perp b$, an orientation in which the magnetic field could sweep through all angles of the (010) plane and where both molecules in the unit cell are magnetically equivalent. Spectra were recorded at 10° intervals starting when H was parallel with [001]. At $\theta \approx 110°$ a sharp spectrum was observed which corresponded to H being perpendicular to the molecular z axis of both molecules in the unit cell. This alignment, shown in Figure 2, corresponds to a field perpendicular to the H_2O–Mn–H_2O axis and within 6° of the D_x axis of both molecules. This determined the two sets of molecular D tensor axes related by the twofold crystallographic screw axis.

The crystal was then oriented with the precession camera so that the field could sweep through the plane containing the two molecular D_z vectors and the [010] axis, the shaded plane in Figure 1. At an orientation corresponding to a magnetic field parallel to a H_2O–Mn–H_2O molecular axis, the D_z spectrum was recorded. Furthermore it will be noted in Figure 1 that the D_y axis is only 5° out of the plane being studied and that spectrum was also recorded. This determined the D tensor relative to the molecular coordinates as shown in Figure 3. The D_x spectrum recorded in the (010) plane is shown in Figure 4. In this orientation the field is not directed along the D_x axis of either molecule but along the bisecting

Table I. Epr Parameters for the Manganese Compounds[a]

	(a) $[Mn(acac)_2(H_2O)_2]$		
g	1.98 (2)[b]	A_y	−90.4 ± 0.5 G
D	702 ± 5 G	A_z	−93.8 ± 0.5 G
E	205 ± 5 G	Q'	−0.7 ± 0.4 G
A_x	−90.3 ± 0.5 G	Q''	0.2 ± 0.2 G
	(b) $[Mn(C_5H_5NO)_6](ClO_4)_2$		
g	2.002 (2)	$B\ (A_x = A_y)$	−90.1 ± 0.5 G
D	410 ± 5 G	Q'	−0.20 ± 0.05 G
E	0 ± 5 G	$\lvert a - F \rvert$	9 ± 5 G
A	−86.3 ± 0.5 G		

[a] Values are reported for X band at room temperature. [b] Overlap of hyperfine lines caused by site splitting in the monoclinic lattice prevented a more precise determination of g.

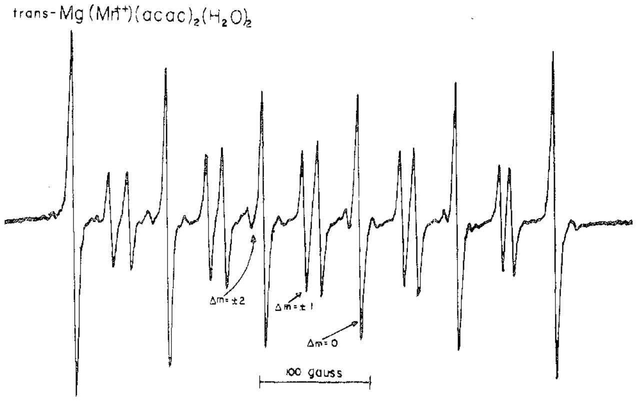

Figure 5. Q-Band liquid nitrogen epr spectrum of $\Delta M = +^1/_2 \rightarrow -^1/_2$ transitions of *trans*-$[Mg(Mn^{II})(acac)_2(H_2O)_2]$ at the orientation $\theta = 88°$, $\phi = 8°$.

vector at 6° from both molecules where they are magnetically equivalent, therefore there appear 10 small intensity-forbidden doublets in addition to the usual 30 hyperfine lines.

The spin-Hamiltonian parameters are listed in Table I. The g value was found to be isotropic within experimental error and was close to the free-spin value of 2.0023. The hyperfine splitting parameters approximate axial symmetry, A_x being very close in magnitude to A_y. After obtaining A_z the sign of D/A_z can be determined by comparing the overall hyperfine separations in the $\pm m \leftrightarrow \pm(m-1)$ transitions at low and high field.[11] This separation is slightly less at low field than at high field so that D/Az must be negative. Assuming A_z to be negative, then D is positive.

Bir, *et al.*, have shown that the behavior of the forbidden nuclear transitions can be predicted by present theories only when the orientation of the magnetic field is close to a principal molecular axis.[23] In order to observe and analyze the so-called forbidden transitions, the D_x orientation was chosen. This was done because the spectrum is uncluttered by site splitting since the two Mn(II) spectra coincide, and also the (010) plane is perpendicular to the needle axis and is easily mounted. In the spectra of the D_y and D_z orientations, the forbidden doublets are unassignable due to the presence of overlap due to site splitting. The absence of data for the forbidden doublets in the D_y and D_z orientations results in the large reported uncertainties in the calculated values of the nuclear electric quadrupole parameters. In Figure 5 is shown the central ΔM $+^1/2 \rightarrow -^1/2$ transition at 77°K with $\theta = 88°$, $\phi = 8°$. The large distortions from cubic symmetry have made possible the observation of nuclear electric quadrupole interaction. Besides the six hyperfine lines with $\Delta m = 0$, there is a group of five doublets with $\Delta m = \pm 1$ and a group of four doublets with $\Delta m = \pm 2$. From the separation of the doublets, Q' the quadrupole coupling constant may be determined. Equation 4 was used for the given angles. Table II gives the experimental and calculated values for δH_d using the values given in Table I.

Table II. Calculated (from Eq 4) and Experimental Values for Separations, δH_d, of $\Delta m = \pm 1$ Doublets[a]

(a) *trans*-$[Mg(Mn^{II})(acac)_2(H_2O)_2]$ ($\theta = 88°$, $\phi = 8°$)

δH_d(exptl)	δH_d(calcd) ($Q' = 0$, $Q'' = 0$)	δH_d(calcd) ($Q' = -0.7$, $Q'' = 0.2$)
29.0	23.3	28.3
24.9	23.4	25.9
23.6	23.5	23.5
21.9	23.6	21.0
18.2	23.7	18.6

(b) $[Zn(Mn^{II})(C_5H_5NO)_6](ClO_4)_2$ ($Q'' = 0$, $E = 0$, $\theta = 8°$)

δH_d(exptl)	δH_d(calcd) ($Q' = 0$)	δH_d(calcd) ($Q' = -0.2$)
20.6	22.9	20.7
22.5	23.4	22.2
23.5	23.8	23.8
25.5	24.2	25.4
26.2	24.6	26.9

[a] Q band, 77°K; all units in gauss.

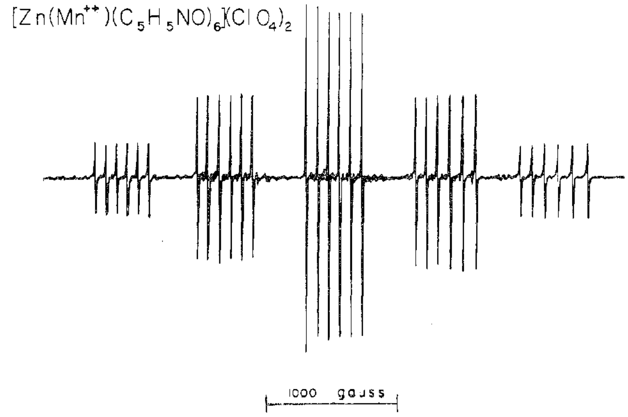

Figure 6. X-Band, room-temperature epr spectrum of $[Zn(Mn^{II})(C_5H_5NO)_6](ClO_4)_2$ oriented with the magnetic field parallel with the molecular z axis of [111] rhombohedral crystallographic axis.

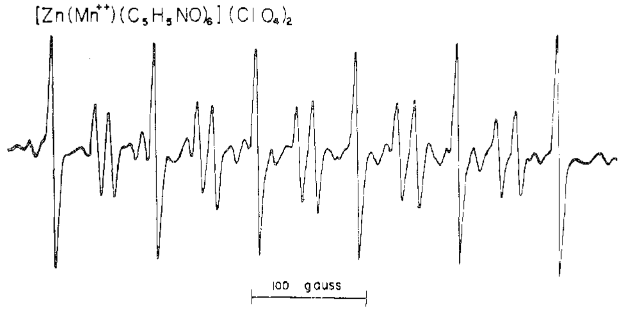

Figure 7. Q-Band, liquid nitrogen epr spectrum of central $\Delta M = +^1/_2 \leftrightarrow -^1/_2$ transitions of $[Zn(Mn^{II})(C_5H_5NO)_6](ClO_4)_2$ with $\theta = 6°$.

The analysis of quadrupole parameters was carried out at Q-band because the third-order effects then become very small and a better fit of the data is obtained.

The interpretation of the $[Zn(Mn^{II})(C_5H_5NO)_6](ClO_4)_2$ spectra was greatly simplified by the fact that there is only one molecule in the unit cell. A spectrum is shown in Figure 6 with the magnetic field H parallel to the molecular z axis. This corresponds to a crystallographic orientation of $\vec{H}$ parallel to the threefold [111] rhombohedral axis or the [001] axis of the hexagonal unit cell. The g value was found to be isotropic and equal to the free-spin value within experimental error. The epr parameters are listed in Table I. The crystal field parameters are in fair agreement with those obtained from recent powder measurements.[24]

An analysis of the forbidden doublets at small angles from the z axis showed a large quadrupole contribution. In Figure 7 a spectrum of the central $\Delta M +^1/_2 \rightarrow -^1/_2$ transition shows the $\Delta m = \pm 1$ transition in addition to the allowed $\Delta m = 0$ transitions. Table II gives the calculated and experimental values for δH_d using the values given.

Experimental values were recorded at Q-band wavelength, but in general, where analyses could be carried out on data obtained at both frequencies, the parameters obtained agree within experimental error.

Discussion

The compound [Mg(acac)$_2$(H$_2$O)$_2$] was chosen as the diamagnetic host lattice for [Mn(acac)$_2$(H$_2$O)$_2$] because both compounds have the same structure and the coordination polyhedron surrounding the metal ions is similar. The molecules are tetragonally distorted, the Mn–O(acac) distance being 2.13 Å while the Mn–O(water) distance is considerably longer, 2.26 Å. The chelate rings form a plane with the manganese ion 0.58 Å out of the least-squares plane, the acac oxygens forming a nearly square plane around the manganese.

A recent investigation of a manganese chelate by Günthard, *et al.*,[3] has reported a large D value (680 G) and the presence of a rhombic term in the crystal field, E = 190 G. The chelate under investigation there, Mn(pic)$_2$(H$_2$O)$_2$, is however highly unsymmetrical and this undoubtedly contributes to the rhombic anisotropy. Other compounds reported that may be chemically related to the acetylacetonate are the formate,[25] Mn(HCOO)$_2$·2H$_2$O, and the acetate, investigated as both a trihydrate[26] and a tetrahydrate.[27] The zero-field splitting is large in both compounds, which are of unknown structure, being about 520 G in the formate and 442 G in Mn(CH$_3$COO)$_2$·4H$_2$O.

For the case of *trans*-[Mn(acac)$_2$(H$_2$O)$_2$] the chelate in the x–y plane is very symmetrical. It has been proposed earlier that the crystal field splittings caused by acetylacetonate ligands are not greatly different from those caused by water.[28] The tetragonal distortion of the water oxygen atoms would explain a D crystal field term, but since the acac oxygens form a nearly square plane, there must be other factors which induce such a large E term. One possibility is that the manganese atom lies not in the plane, but above it. We further propose that the symmetry of the D tensor is due to charge accumulation in the x–y plane and that further charge accumulation occurs along the x axis due to electron delocalization on the chelate ring. The chelate ring has empty p_z' orbitals and a near-planar configuration, fulfilling the criteria for delocalization. The quasiaromatic nature of the chelate ring also agrees with the anisotropy reported from quadrupole investigations on Cu(acac)$_2$ by Rollmann and Chan.[29] It will be noted that the D term for *trans*-[Mn(acac)$_2$(H$_2$O)$_2$] is quite large, in fact approaching the upper bound of values reported by epr investigation.

This is the only manganese chelate which has allowed the determination of nuclear electric quadrupole parameters, and the spectra of neither the formate nor the acetate exhibit a nuclear electric quadrupole splitting. The negative value of Q' in the compound points to the fact that there is a tetragonal charge accumulated in the x–y plane, in agreement with our theory of the magnitude of the D term. The value of Q' is larger in magnitude than that of many ionic compounds; for example, $Q' = -0.7$ G may be compared with $Q' = -0.35$ G for manganese in calcium tungstate, CaWO$_4$.[30] The value of Q' may also be compared with that for manganese in Al$_2$O$_3$ (+1.0 G),[16] β-Ga$_2$O$_3$ (+0.9 G),[22] and ZnO (+0.15 G).[31]

The single-crystal epr study of [Zn(Mn^{II})(C$_5$H$_5$NO)$_6$]-(ClO$_4$)$_2$ yields results in reasonable agreement with the powder studies of Woltermann and Wasson.[24] However, the use of single crystals enabled us to obtain much more information concerning nuclear and crystal field effects. The D value of 410 G is quite large when one considers that this is an octahedral coordination polyhedron with all ligands identical. We believe that the large D value is due to a combination of steric trigonal distortions due to crystal packing of molecules and also the axial location of the anionic charge of the perchlorate ions. The pyridine *N*-oxide ligands are quite large and this may add to the steric effects of crystal packing; also, the Mn–O–N bonds are expected to be nonlinear, causing a relatively low local symmetry. The large deviation from cubic symmetry enables us to observe a nuclear electric quadrupole effect. The magnitude of this indicates a more covalent type of bond between the ligands and the central ion.

That Q' is negative in [Mn(C$_5$H$_5$NO)$_6$](ClO$_4$)$_2$ leads us to believe that the quadrupolar coupling is sensitive to the immediate ligand field of the molecule. The six pyridine *N*-oxide molecules are sterically compressed by trigonal packing forces. This results in a ligand field accumulation in the x–y plane which is felt by the nucleus. The dependence of the quadrupolar coupling constant Q' on the quadrupolar moment is dependent on the quadratic axial crystal electric potential and the Sternheimer antishielding factor;[22,32] both are functions which decrease as the distance from the nucleus increases. Therefore little information is delivered to the manganese nucleus by the distant perchlorate anions.

A recent discussion[4] of copper chelates suggests that Q' should be smaller in a covalent compound than an ionic one. This description refers to the bonding nature of the ligand with the metal. The smaller value of Q' in [Mn(C$_5$H$_5$NO)$_6$](ClO$_4$)$_2$ indicates a more covalent bond between the metal ion and the surrounding ligands while the large value of Q' in *trans*-[Mn(acac)$_2$(H$_2$O)$_2$] indicates a more ionic bond between the central metal ion and its acetylacetonate ligands.[33]

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Registry No. *trans*-[Mg(acac)$_2$(H$_2$O)$_2$], 53447-39-5; *trans*-[Mn(acac)$_2$(H$_2$O)$_2$], 29259-29-8; [Zn(C$_5$H$_5$NO)$_6$](ClO$_4$)$_2$, 23195-17-7; [Mn(C$_5$H$_5$NO)$_6$](ClO$_4$)$_2$, 23608-36-8.

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(33) **Note Added in Proof.** The crystal structures of manganese acetate tetrahydrate [E. F. Bertaut, T. Q. Duc, P. Burlet, P. Burlet, M. Thomas, and J. M. Moreau, *Acta Crystallogr., Sect. B*, **30**, 2234 (1974)] and [$Ni(C_5H_5NO)_6$](BF_4)$_2$ [A. D. van Ingen Schenau, G. C. Verschoor, and C. Romers, *ibid.*, **30**, 1686 (1974)] have been reported.

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Synthesis and Characterization of Manganese Complexes Containing a Synthetic Macrocyclic Ligand

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A number of manganese(II) and -(III) complexes with the uncharged 14-membered macrocyclic ligand, *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ([14]aneN_4) have been synthesized and fully characterized. The Mn(II) compounds are oxygen sensitive and are easily destroyed by exposure to pH extremes. The manganese(III) complexes appear to be air stable and less sensitive to pH effects than the Mn(II) derivatives. The solid-state esr spectra of the divalent complexes indicate that the metal ion is experiencing a relatively small tetragonal distortion. The observed tetragonal spitting parameter, *D*, is 0.1–0.2 cm^{-1}. Chemical and electrochemical investigations show that the Mn^{III}–[14]aneN_4 complexes are easier to reduce than a number of manganese(III)–porphyrin complexes. These complexes also display magnetic moments and electronic absorption bands consistent with high-spin, tetragonally distorted d^4 systems.

Introduction

Although complexes of many cyclic tetraaza ligands have been prepared with a variety of transition metal ions,[2] there have been few reports of Mn complexes of this type. This kind of ligand possesses a number of readily accessible structural features which can serve to alter the chemistry of the coordinated metal ion. The availability of various macrocyclic frameworks coupled with the number of obtainable oxidation states for manganese[3] emphasizes the possibility of these systems as useful redox agents. In this regard it has been shown[4] that a manganese(II) complex containing the cyclic ligand, phthalocyanine, is effective in converting cyclohexadiene to benzene in the presence of nitrobenzene. Manganese(II) phthalocyanine and oxygen gas have also been employed in the oxidation of cumene to cumene hydroperoxide.[5] The specific function of the complex in these systems is essentially unknown. Perhaps most interesting is the role manganese macrocyclic complexes may play in plant[6] as well as animal[7] physiology. Although there is no direct evidence for the existence of manganese–porphyrin complexes in the photosynthetic process, Calvin[6] has suggested that they may be essential to oxygen evolution. Manganese–porphyrin complexes under certain conditions are themselves photoactive and conversion between the II, III, and IV oxidation states may be important in the oxygen evolution part of the cycle.

As part of a study to examine the chemistry of manganese macrocyclic systems as a function of ligand structure, we have synthesized a number of manganese(II) and -(III) complexes with *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, [14]aneN_4,[8] Figure 1. This ligand is a saturated, tetradentate, uncharged macrocycle which can be easily synthesized in gram quantities.[9] Furthermore, its stereochemistry has been extensively documented and planar coordination is preferred.[10]

Experimental Section

Reagents and Equipment. All of the chemicals used were reagent grade unless otherwise noted. A Vacuum Atmospheres controlled-atmosphere drybox was used for the synthesis of the manganese(II) complexes. Solution absorption spectra were recorded using a Cary 14 spectrophotometer. Solid-state mull spectra were obtained using filter paper impregnated with Halocarbon 25-S5 grease and the compound. The absorption spectrum (4.3–30 kK) was recorded at 77°K in a manner previously described.[8]

The esr spectra between 500 and 8500 G were obtained using a Varian E-9 spectrometer operating at a microwave energy of 0.316 cm^{-1}. The $CF_3SO_3^-$ and $CH_3CO_2^-$ derivatives were run as undiluted powdered samples at room temperature.

Infrared spectra were obtained on Nujol mulls between KBr disks using a Perkin-Elmer 521 spectrophotometer. Polyethylene plates were used for measurements below 400 cm^{-1}. Conductivities at room temperature on 10^{-3}–10^{-4} *M* solutions were obtained using a Yellow Springs Instrument Co. Model 31 conductivity bridge. Magnetic moment measurements were done on 10–20 mg of sample in the solid state using the Faraday method.[11] The diamagnetic correction for [14]aneN_4 as determined was -254×10^{-6} cgsu.

The electrochemistry was carried out under nitrogen in acetonitrile. The polarographic and cyclic voltammetric behavior of the Mn(II) derivatives was examined with dropping mercury and hanging mercury drop electrodes, respectively. A platinum electrode was used for the Mn(III) complexes. Solutions were 10^{-3} *M* in complex and 0.10 *M* in tetra-*n*-butylammonium perchlorate as the supporting electrolyte. All potentials were determined at room temperature *vs.* an Ag-AgCl (sat NaCl) reference electrode. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Instranal Laboratories, Rensselaer, N. Y.

Preparation of [14]aneN_4. The synthesis of this ligand has been previously described.[9] For all the manganese syntheses the free ligand was dried for 2 days under vacuum (0.02 mm) over P_4O_{10}. The absence of water was checked using infrared spectroscopy.

Synthesis of Mn^{II}[14]aneN_4(SO_3CF_3)$_2$. The metal salt $Mn(SO_3CF_3)_2 \cdot CH_3CN$ necessary for the synthesis of the complex was synthesized from manganese metal and HSO_3CF_3 in acetonitrile. Thus, to 20 g of anhydrous HSO_3CF_3 in 400 ml of rapidly stirred acetonitrile was added 10.0 g of manganese metal (60 mesh). The stirred suspension was heated to 60° under nitrogen for 2 hr. After filtering the cool solution with the help of filter aid, the volume was reduced to 100 ml. Addition of 800 ml of ether, which was dried with $LiAlH_4$, caused the precipitation of the white hygroscopic manganese(II) salt. The salt was removed by filtration, and dried over P_4O_{10} under vacuum. The yield was 10.5 g. Although three elemental analyses showed variable composition, infrared evidence coupled with