Electron Spin Resonance Study of Manganese(II) doped into Hexakis-(4-methylpyridine *N*-oxide)-zinc, -cadmium, and -mercury Perchlorates

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The powder e.s.r. spectra of mangenese(II) ions doped into $[M(4Me\text{-}pyo)_6][ClO_4]_2$ (M = Zn, Cd, or Hg; 4Me-pyo = 4-methylpyridine *N*-oxide) have been interpreted by exact diagonalisation of a spin-Hamiltonian matrix. The *D* values decrease slightly (from 0.063 to 0.059 cm^{-1}) with increasing size of the host metal ion, while λ is constant (0.06) within the series. Spin-forbidden transitions, particularly those in the *yz* plane, contribute significantly to the observed spectra.

IN recent years e.s.r. spectroscopy has been shown [1,2] to be a useful tool in determining the stereochemistry of manganese(II) complexes. However, few attempts [3] have been made to assess the potential of this ion as a stereochemical probe for those bivalent metal ions which, because of an empty or completely filled *d* shell, are not amenable to study by the usual physical techniques. Recent e.s.r. work on Mn^{II} doped into the hexakis complexes of zinc, cadmium, and mercury with substituted pyridine *N*-oxides [4,5] is therefore of interest. Rather surprisingly, the zero-field splitting parameters, *D* and *E*, found [4,5] show no correlation with the size of the host metal ion, or with the steric and electronic properties of the pyridine-ring substituents. Within the 4-methylpyridine *N*-oxide (4Me-pyo) series, for example, the variation in *D* was only 12%, while $\lambda (= E/D)$ ranged from 0 in the cadmium complex to 0.23 for the mercury complex, with an intermediate value for the zinc complex.

We have reinvestigated the spectra of the 4Me-pyo complexes at both *X*- and *Q*-band frequencies, and find that some of the parameters obtained deviate considerably from the published values.

RESULTS AND DISCUSSION

The interpretation of the e.s.r. spectra of d^5 systems in the polycrystalline state has been dealt with by several workers, and the usefulness of the 'simplified' spin Hamiltonian (1), in which the quartic spin operators are omitted, has been amply demonstrated. Both *A*

$$\mathcal{H} = g\beta BS + D(S_z^2 - \tfrac{1}{3}S^2) + E(S_x^2 - S_y^2) + SAI \quad (1)$$

and *g* are assumed to be isotropic, with the latter equal to 2.00. {In a recent single-crystal study [2] of $[Zn(Mn)(pyo)_6][ClO_4]_2$ the isotropic *g* value was found to be equal to the free-spin value of 2.002.}

Previously,[4,5] *D* and *E* for the 4-Me-pyo complexes were obtained using first-order perturbation theory. In this work a first estimate was made in this way, but it was then refined by exact diagonalisation of a spin-Hamiltonian matrix based on (1), but omitting the hyperfine-interaction term. The calculated energy levels were scanned using the program [6] ESRS. As only two parameters were to be determined, the fitting procedure was carried out over the outer transitions only; no attempt was made to analyse the exceedingly complex $g_{eff.} = 2$ region.

In Tables 1 and 2, which list the observed spectra for the mercury complex, together with the calculated resonance fields, only the most prominent observed peaks are given for the 0—200 mT region. The notation

TABLE 1

X-Band spectrum (mT) of $[Hg(Mn)(4Me\text{-}pyo)_6][ClO_4]_2$

	Calculated			
Observed [a]	for $D = 0.059\ cm^{-1}$, $\lambda = 0.06$		for [b] $D = 0.067\ cm^{-1}$, $\lambda = 0.23$	
ca. 90.1w [c]	88.3	e_z	60.76	e_z
ca. 125.6w	*d*		121.9	a_y
ca. 130.5w	*d*			
206.3m	208.6	a_y	202.5	d_z
	214.3	d_z	224.4	b_y
	254.5	a_x		
260.2m	261.6	b_y		
	278.7	b_x		
			401.8	e_x
451.6m	452.4	e_x	443.2	d_y
466.0m	466.5	b_z	477.2	b_z
493.7ms	495.2	e_y		
589.3w	593.3	a_z	586.5	e_y
			628.6	a_z

[a] $\nu = 9.531$ GHz. [b] Parameters from ref. 5. [c] Line positions are taken as the mean of the third and fourth components of the hyperfine multiplet. This causes small errors at low field where second-order effects are most important, *e.g.* errors may be as great as 4 mT at 120—130 mT. [d] Assigned as forbidden transition (see text).

TABLE 2

Q-Band spectrum (mT) of $[Hg(Mn)(4Me\text{-}pyo)_6][ClO_4]_2$

	Calculated			
Observed [a]	for $D = 0.059\ cm^{-1}$, $\lambda = 0.06$		for [b] $D = 0.067\ cm^{-1}$, $\lambda = 0.23$	
			991.6	e_z
1 029m	1 024.8	e_z	1 038.0	a_y
1 134ms	1 131.5	a_y	1 133.2	d_z
1 154ms	1 151.0	d_z	1 153.9	b_y
	1 177.7	a_x		
1 201s	1 199.9	b_y		
1 223s	1 221.6	b_x	1 239.3	a_x
1 323s	1 324.4	d_x	1 327.6	e_x
1 348s	1 348.1	d_y		
	1 384.2	e_x	1 395.1	d_y
1 404ms	1 403.7	b_z	1 419.6	b_z
1 430ms	1 428.8	e_y		
1 532m	1 530.2	e_z	1 521.8	e_y
			1 565.1	a_z

[a] $\nu = 35.76$ GHz. [b] Parameters from ref. 5.

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[3] M. Goodgame and P. J. Hayward, *J. Chem. Soc.* (*A*), 1971, 3406.

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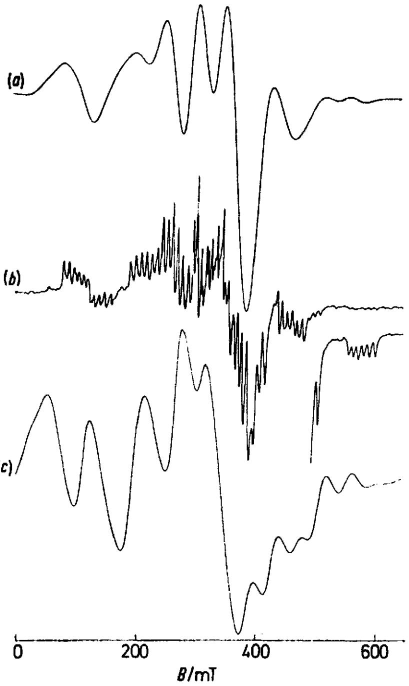
[5] G. M. Woltermann and J. R. Wasson, *J. Phys. Chem.*, 1974, **78**, 45.

[6] D. Vivien and J. F. Gibson, *J.C.S. Faraday II*, 1975, 1640.

a—*e* for the M values is according to ref. 7. Calculated single-crystal transition probabilities are in each case close to the 5 : 8 : 9 : 8 : 5 ratio required by first-order perturbation theory,[8a] and are not listed in the Tables. The spectra of the zinc and cadmium complexes were very similar and resonance fields are not tabulated here. In every case agreement with predicted fields was generally very good, and markedly better than for the previously assigned parameters, especially at Q-band frequency. For the zinc complex the fit for the spin-allowed bands was approximately equally good for λ values of 0.06 and 0.07. However, the value of 0.06 gave better agreement for the spin-forbidden bands.



E.s.r. spectra (9.531 GHz) of $[Hg(Mn)(4Me\text{-}pyo)_6][ClO_4]_2$: (*b*) experimental; (*a*) and (*c*) computer-simulated line shapes for parameters $D = 0.059$ cm^{-1} and $\lambda = 0.06$ and $D = 0.067$ cm^{-1} and $\lambda = 0.23$ respectively, using 93 angles per octant in the icosahedral approximation (see refs. 6 and 9)

Simulated random-orientation spectra, excluding hyperfine splitting, were plotted for both sets of parameters using the program[9] SHAPE 9; a Gaussian line shape was assumed and the isotropic peak-to-peak linewidth of the first-derivative spectra was taken as 30.0 mT. For the mercury complex, the experimental and calculated traces are compared in the Figure. Of the two sets of parameters, $D = 0.059$ cm^{-1} and $\lambda = 0.06$ gives much the better fit, at least over the outer transitions. The linewidth was chosen to suit these outer transitions, and the fit is therefore less good for the lines near $g_{\text{eff.}} = 2$, which are narrower since the resonance fields are less sensitive to the small variations in parameters caused by crystal imperfections.[8b]

Woltermann and Wasson[4,5] do not list resonance fields for any of the complexes. Their published spectrum of the mercury complex is generally similar to ours, although there are some intensity differences, and the lowest-field transition seems to be at slightly higher field in our spectrum. The difference in interpretation arises largely from their failure to identify the weak bands between 100 and 160 mT in all the three complexes as spin-forbidden ($\Delta M_s \neq \pm 1$) transitions, which have zero probability when the field is parallel to the principal axes. Aasa[10] stated that stationary values of $B(\theta,\phi)$, which are associated with the appearance of lines in the powder spectrum, occur only when the magnetic field lies in one of the principal planes. Calculations for the mercury complex show that the sextets centred on *ca.* 125 and *ca.* 130 mT may be ascribed respectively to the 5–2 transition $[-\frac{1}{2}(-\frac{5}{2},\frac{1}{2})\rightarrow\frac{3}{2}(\frac{1}{2},\frac{5}{2})]$ in the yz plane (with possibly a small contribution from 5–2, zx) and to 5–3 $[-\frac{3}{2}(\frac{1}{2},-\frac{1}{2})\rightarrow\frac{5}{2},\frac{1}{2}(-\frac{3}{2},-\frac{1}{2})]$ in yz (Table 3). All these transitions have $\Delta M_I = 0$; calculations were also made for higher ΔM_I, but the transition probabilities were two or more orders of magnitude lower than for the 'nuclear-allowed' lines. Despite its rather low transition probability relative to the $\Delta M_s = 1$ bands, the observed peak height of the 5–2(yz) transition in all three complexes is comparable with that of e_z, presumably chiefly on account of the sinθ weighting factor in the expression for the intensity of a powder line. For compounds of comparable D, such 'half-field' transitions for the manganese(II) ion have previously been analysed numerically (neglecting off-diagonal hyperfine terms) only for the case of Mn$^{\text{II}}$ in tremolite[11] (D 0.042 cm^{-1}, λ 0.19).

Neglect of the spin-forbidden transitions might appear

TABLE 3

Analysis of the 110—160 mT region of the X-band spectrum of $[Hg(Mn)(4Me\text{-}pyo)_6][ClO_4]_2$

	$B_{\text{res.}}$ calc. for $\nu = 9.531$ GHz, $D = 0.059$ cm^{-1}, $\lambda = 0.06$		
	$\theta = 30$, $\phi = 0°$	$\theta = 30$, $\phi = 90°$	$\theta = 80$, $\phi = 90°$
$B_{\text{res.}}$ (obs.)	Transition[a] 2–5	2–5	3–5
±0.5 mT	t.p.[b] = 0.7—0.8	0.8	0.08
ca. 114.0s	113.9 ($-\frac{1}{2}$)[c]		
		115.4 ($-\frac{3}{2}$)	
117.6w			118.3 ($-\frac{3}{2}$)
122.8s	122.8 ($+\frac{1}{2}$)	123.4 ($-\frac{1}{2}$)	
126.4w			126.7 ($-\frac{1}{2}$)
131.9s	132.1 ($+\frac{3}{2}$)	132.2 ($+\frac{1}{2}$)	
135.3w			135.8 ($+\frac{1}{2}$)
141.5s	141.8 ($+\frac{5}{2}$)	141.9 ($+\frac{3}{2}$)	
145.1w			145.4 ($+\frac{3}{2}$)
151.6s		152.4 ($+\frac{5}{2}$)	
155.2w			155.7 ($+\frac{5}{2}$)

[a] The spin levels are labelled 1—6 in order of decreasing energy (see text for indication of the wavefunctions involved). [b] t.p. = Transition probability calculated as in R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, 1969, **50**, 294 and relative to that of a_z and e_z as 5. [c] Values of M_I are given in parentheses.

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[9] R. M. Butterworth, J. F. Gibson, and E. M. Price, unpublished work.

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to be validated by the single-crystal study[2] of [Zn(Mn)-$(\mathrm{pyo})_6$][$\mathrm{ClO_4}$]$_2$, which gave parameters in fairly good agreement with those from the powder spectrum. However, this result is somewhat fortuitous since, for the particular parameters concerned (D 0.039 cm^{-1}, λ 0), the strongest spin-forbidden transition (4–2, centred on 187 mT in the yz plane) partially overlaps e_z (177 mT at 9.5 GHz).

No attempt was made in the present work to analyse spin-forbidden transitions between 0 and 100 mT, the components of which are interspersed with those of e_z. Additional transitions between non-adjacent levels are predicted up to *ca.* 350 mT, but are presumably buried under the much stronger allowed transitions. We are, however, unable to account for a band which appeared at 478 mT in the X-band spectrum of the zinc complex, although no 'extra' absorption corresponding to this could be detected at Q-band frequency.

In the Q-band spectrum the spin-forbidden lines appeared only at 300—500 mT, *i.e.* well out of the range of the allowed transitions, and, as the spin levels involved are characterised by almost pure wavefunctions, their transition probabilities are quite low. In addition, location of the centre of each group of six hyperfine lines is far easier at the higher frequency, where the hyperfine components were almost equally spaced. The determination of A by computing the average of all the hyperfine separations is also best performed at Q band. For all the three complexes, the magnitude of A calculated in this way is 8.9 mT (= 0.008 32 cm^{-1}). This differs from the value (9.5 mT) given by Woltermann and Wasson[5] by more than the difference between all their compounds, and it seems that such small variations should be viewed with caution when measured at X band only.

The relative signs of A and D are readily determined by comparison (at X band) of the mean spacing of the hyperfine lines in the $\pm\frac{3}{2} \longleftrightarrow \pm\frac{5}{2}$ transitions when B is parallel to z. In all the three complexes this spacing was greater for the highest observed transition than for the lowest allowed band; thus if A is negative, as is usually the case for Mn$^{\mathrm{II}}$, these transitions correspond respectively to $-\frac{3}{2} \longleftrightarrow -\frac{5}{2}$ and $\frac{3}{2} \longleftrightarrow \frac{5}{2}$, and D is positive, as in [Zn(Mn)$(\mathrm{pyo})_6$][$\mathrm{ClO_4}$]$_2$.[2]

The D values (Table 4), while not greatly different from those reported earlier,[4,5] do lie in the inverse order of the ionic radii of the host metal, a result which has been obtained previously for at least two different series of isomorphous compounds, doped with either manganese(II)[12] or gadolinium(III).[13] Moreover, λ is constant throughout the 4Me-pyo series.

TABLE 4

Zero-field splitting parameters for the complexes

	This work		Refs. 4 and 5	
Host metal	D $\pm$0.001 cm^{-1}	λ $\pm$0.01	D/cm^{-1}	λ
Zn	0.063	0.06	0.072	0.188
Cd	0.061	0.06	0.064	0.0
Hg	0.059	0.06	0.067	0.23

It is clear that, even for values of $D/h\nu$ as low as 0.2, low-field spin-forbidden transitions have *powder* intensities comparable with those of the $\Delta M_s = 1$ bands, and numerical solution of the spin Hamiltonian, followed by a search for all the possible transitions within the manifold of spin levels, is essential for accurate assignment of spectral lines.

EXPERIMENTAL

The yellow crystalline complexes precipitated immediately on addition of ethanolic solutions of the hydrated metal perchlorates to a slight stoicheiometric excess of the ligand (mol ratio *ca.* 1 : 7) in the same solvent. All the three solids are light-sensitive, and spectra were therefore run on freshly prepared samples. Analytical results were obtained by the Microanalytical Laboratory, Imperial College (Found: C, 47.7; H, 4.6; N, 9.2. Calc. for $\mathrm{C_{36}H_{42}Cl_2N_6O_{14}Zn}$: C, 47.1; H, 4.6; N, 9.1. Found: C, 44.7; H, 4.5; N, 8.9. Calc. for $\mathrm{C_{36}H_{42}CdCl_2N_6O_{14}}$: C, 44.8; H, 4.4; N, 8.7. Found: C, 41.2; H, 4.0; N, 8.1. Calc. for $\mathrm{C_{36}H_{42}Cl_2HgN_6O_{14}}$: C, 41.0; H, 4.0; N, 8.0%).

The e.s.r. spectrometers have been described previously.[6] All the spectra were obtained on polycrystalline samples at room temperature.

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