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Electron Spin Resonance Spectra of Manganese(II) Ions in *cis*-Mg(diketone)$_2$L$_2$ Environments

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Powder e.s.r. spectra are reported for manganese(II) ions doped into cis-*Mg(dibenzoylmethane)$_2$(dimethylformamide)$_2$ and Mg(hexafluoroacetylacetone)$_2$(H$_2$O)$_3$, and zero field splitting parameters D and λ (= E/D) are derived. In each case D is negative, and considerably smaller than in* trans-*Mg(acetylacetone)$_2$(H$_2$O)$_2$. The rhombicity is also lower in the* cis-*complexes, and it seems that a stereochemical criterion based on these parameters may be possible.*

Introduction

Adducts of metal β-ketoenolates, M^{II}(diketone)$_2$L$_2$, where L is a monodentate ligand, may have either *cis*- or *trans*-stereochemistry, several examples of each being known. In principle, the two configurations may be distinguished by vibrational spectroscopy, but with such complicated ligands this technique is fraught with difficulty.

As part of our investigations into the use of manganese(II) as a stereochemical probe for complexes of group(II) metal ions, we considered it worthwhile to assess whether the powder e.s.r. spectra of manganese-doped complexes can be used to distinguish *cis*- from *trans*-stereochemistry.

At the simplest level, the zero-field splitting for a *trans*-complex is expected to be double that for an analogous *cis*-complex and opposite in sign. However, a recent single-crystal e.p.r. study [1] of *trans*-Mg(Mn)(acac)$_2$(H$_2$O)$_2$ showed the D-tensor to be strongly rhombic, and it is clear that simplistic interpretations are of no value. Moreover, with powder spectra it is not always possible to determine the sign of the splitting.

We report here a study of manganese(II) in *cis*-Mg(dbm)$_2$(dimethylformamide)$_2$ (where dbm = dibenzoylmethane) and in Mg(hfac)$_2$(H$_2$O)$_3$ (hfac = hexafluoroacetylacetone) of unknown configuration. Attempts to prepare the corresponding dihydrate were unsuccessful, but the infrared spectrum of the trihydrate showed no "unbonded" C=O groups, a single sharp band being observed in the ν(C=O) region.

Experimental

Mg(Mn)(dbm)$_2$(DMF)$_2$ was prepared by the method of Hollander *et al.* [2] using 1 mol percent manganese chloride with the magnesium salt. *Anal.* Found: C, 70.7; H, 5.8; N, 4.7. Calc.: C, 70.1; H, 5.9; N, 4.5%.

TABLE I. E.s.r. Spectra (mT) of Mg(Mn)(dbm)$_2$(DMF)$_2$; a, b, d and e Transitions.

Observed		Calculated for D = –0.022 cm^{-1}, λ = 0.13		
ν = 35.740 GHz	ν = 9.531 GHz	B (Q-band)	B (X-band)	Axis, levels
1183 w	246 w	1183	246.4	a_z
1212 ms	277 ms	1212	276.6	e_y
1233 s		1230	293.3	b_z
	305 s		306.6	d_y
		1306	371.0	a_x
	371 s	1309	371.4	b_y
1318 s		1324	387.4	d_z
1341 ms	404 ms	1343	406.9	a_y
1369 w	434 w	1371	434.8	e_z

TABLE II. E.s.r. Spectra (mT) of $Mg(Mn)(hfac)_2 \cdot 3H_2O$.

Observed		Calculated for $D = -0.038$ cm^{-1}, $\lambda = 0.18$		
ν = 35.840 GHz	ν = 9.531 GHz	B Q-band	B X-band	Axis, levels
	115w[a]			
	127w[a]			
1114w	179w	1118	179.1	a_z
1157ms	221ms	1156	220.7	e_y
1199s	258s	1199	259.0	b_z
1216vs	274vs	1217	276.1	d_y
	325.9		326.5	c_x
	332.9		333.6	c_y, c_{xy}
	338.6		338.8	c_z
	400.2vs		397.6	b_y
1363s	418ms	1361	420.8	d_z
1406ms	466ms	1406	467.9	a_y
1443w	501w	1443	503.6	e_z

[a] $\Delta M_s \neq 1$ transitions.

TABLE III. *c* Transition (mT) of $Mg(Mn)(dbm)_2(DMF)_2$ at X-band.

Observed (ν = 9.531 GHz)	Calculated for $D = -0.022$ cm^{-1}, $\lambda = 0.13$	
	B	Axis
335.3 sh	335.9 sh	x
337.1 div	337.6 div	y, xy pl.
339.9[a]	339.9 sh	z
342.8[a]	343.6 div	zx pl.
	348.2 sh	yz pl.

[a] Not clear whether shoulder or divergence.

$Mg(Mn)(hfac)_2 \cdot 3H_2O$ was prepared by the method described [1] for $Mg(acac)_2 \cdot (H_2O)_2$, again using a 1% nominal doping. *Anal.* Found: C, 24.6; H, 1.6. Calc.: C, 24.4; H, 1.6%.

All spectra were obtained on polycrystalline samples at room temperature. The spectrometers have been described previously [3].

Results

Reference has been made previously [4] to the "simplified" spin Hamiltonian for manganese(II) and the computer program ESRS employed in the spectral analysis.

Both complexes give exceedingly well-defined spectra over the entire range of absorption, ΔB_{pp} in the $g_{eff} = 2$ region being less than 1 mT. The zero field splitting parameters may therefore be obtained to a high degree of accuracy. The fine structure resonance fields were measured at the centres of gravity of the hyperfine sextets, it being assumed that second order hyperfine interactions would not significantly affect their positions. First order perturbation formulae yielded estimates of D and λ (= E/D) which were then refined by comparing the experimental resonances with fields calculated by exact diagonalisation of the spin Hamiltonian matrix (Tables I, II). The notation a–e for the transitions is that of Chatelain and Weeks [5].

In both cases it was possible to determine the sign of D from measurements of differences in the spacing of the hyperfine components of the $\pm\frac{3}{2} \rightarrow \pm\frac{5}{2}$ transitions. In each case the spacing on the lowest allowed transition (a_z in Tables I, II) was greater than that on the highest band (e_z). Assuming that A is negative, as is usually the case for manganese(II) the lowest transition is then $-\frac{5}{2} \leftrightarrow -\frac{3}{2}$, and D is negative. Assignments of transitions a–e in the tables are for negative D.

A more detailed analysis of the C transition, which is isotropic as far as terms linear in the fine structure parameters, was attempted for $Mg(Mn)(dbm)_2(DMF)_2$ at X-band. The powder pattern for this transition was calculated using second order perturbation theory, assuming an isotropic g-tensor and the absence of nuclear hyperfine interaction [6, 7]. We would draw attention to an error in ref. 7 which gives the location of the low-field divergence for $\frac{1}{9} < \lambda < \frac{1}{3}$ as $-8(1 - 3\lambda)^2$; the correct expression is $-8[1 - (3\lambda)^2]$. The observed and calculated fields are compared in Table III. For $Mg(Mn)(hfac)_2 \cdot 3H_2O$, only three components of this transition were resolved, and the analysis is included in Table II. Both compounds showed corresponding strong absorption near 1280 mT in the Q-band spectrum, but overlapping of

TABLE IV. Zero Field Splitting Parameters for Mn^{II} in some Chelated MO_6 Environments.

Host	D (cm^{-1})	λ	Ref.
$[Mg(dbm)_2(DMF)_2]$	−0.022 ± 0.001	0.13 ± 0.01	This work
$Mg(hfac)_2 \cdot 3H_2O$	−0.038 ± 0.001	0.18 ± 0.01	This work
$[Mg(acac)_2(H_2O)_2]$	+0.060	0.29	1
$[Zn(OAc)_2(H_2O)_2]$	+0.023	0.10	8
$Zn(OAc)_2 \cdot 3H_2O$	0.024	0.11	10
$Cd(OAc)_2 \cdot 3H_2O$	+0.032	0.10	11

the components was too severe to permit detailed analysis.

Discussion

The zero-field splitting parameters for the complexes are compared in Table IV with results for other MnO_6 chelated complexes. As expected, the D value for *cis*-$Mg(Mn)(dbm)_2(DMF)_2$ is much smaller than that for *trans*-$Mg(Mn)(acac)_2(H_2O)_2$. The fine structure parameters for the *cis* complex are remarkably close to the values observed [8] in *cis* octahedral $Zn(OAc)_2(H_2O)_2$ despite the much higher angular distortion of the coordination polyhedron in the acetate where the angles O–M–O range between 61° and 103° [9]. Both these complexes, crystallize in space group C2/c, with Z = 4, and the molecules are required to have C_2 symmetry; the two-fold axis coincides for the parameters listed in ref. 8, with D_y (and presumably g_y) in $Zn(Mn)(OAc)_2(H_2O)_2$. For the latter complex, D and E as given in ref. 8 are of opposite sign and are evidently not referred to a 'proper' coordinate axis system. We note, however, that simple interchange of x and y, giving the orientation of Fig. 1, reverses the sign of E leaving D unchanged; this is the proper system of axes in which, for this complex, D and E are both positive. The parameters [10] of $Zn(Mn)(OAc)_2 \cdot 3H_2O$ (Table IV) are so similar to those of the dihydrate as to suggest identical molecular structures for the complexes, and that of the cadmium complex [11] is probably similar.

As the axial zfs in $Mg(Mn)(hfac)_2 \cdot 3H_2O$ lies within the range of values given by the MO_6 chromophores of Table IV, it is likely that two of the water molecules are coordinated to give basically octahedral microsymmetry at the metal ion. D is substantially lower than in *trans*-$Mg(Mn)(acac)_2(H_2O)_2$, however, and λ lies in the intermediate region of the range of values (0–0.33) available to this parameter in a proper coordinate system. The similarity with $Mg(Mn)(dbm)_2(DMF)_2$ and $Zn(Mn)(OAc)_2(H_2O)_2$ is evident, and strongly indicates a *cis* arrangement of ligands in $Mg(hfac)_2 \cdot 3H_2O$. The negative sign for D in $Mg(Mn)(hfac)_2 \cdot 3H_2O$ is then readily explicable on the basis of the same axis system as in Fig. 1, since the $Mg–OH_2$ bond length (which is 2.15 Å in $Mg(acac)_2(H_2O)_2$) is expected to exceed Mg–hfac (2.06 in $Mg(hfac)_3$) by ~0.1 Å; this is also the probable reason for the larger D compared with $Mg(Mn)(dbm)_2(DMF)_2$ in which Mg–dbm = 2.056 and Mg–DMF = 2.095 [2]. On present evidence, therefore, it appears that in this class of molecules with C_2 symmetry a positive value of D is associated with elongation in the z-direction, and *vice versa*; unfortunately, no theoretical prediction of the sign of D in this symmetry is available for comparison with the experimental results.

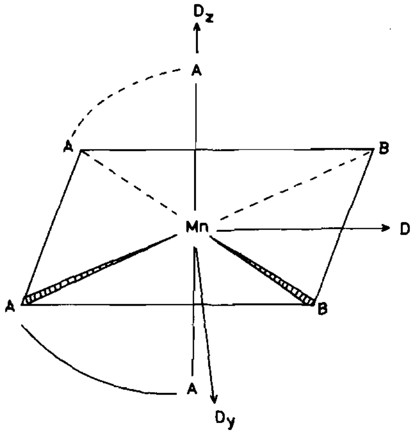

Fig. 1. Presumed orientation of the D-tensor in *cis*-MA_4B_2 complexes.

The value of λ also appears to be consistently smaller in the *cis*-compounds than in *trans*-$Mg(Mn)(acac)_2(H_2O)_2$. This is in accord with the suggestion [1] that the strongly rhombic zero-field-splitting of the *trans* compound is due to the charge accumulation along the x-axis (see Fig. 3 of ref. 1) that results from metal–ligand d_π–p_π overlap. In the *cis*-complexes the π-interactions are not localised along one axis, and the x and y directions should have a more similar electron distribution.

At a more general level, this work shows that even for D values as low as 0.02 cm^{-2}, an accurate evaluation of the zero field splitting parameters is possible from powder spectra. At this low value of D, no spin-forbidden bands were present to complicate the interpretation. However with D of 0.038 cm^{-1} (*i.e.*, $D/h\nu$ about 0.1 at X-band) such spin-forbidden transitions occurred with intensity comparable with that of the outermost spin-allowed transitions. It seems, therefore, that the possibility of such transitions should always be borne in mind when interpreting powder spectra.

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References

1 C. J. O'Connor and R. L. Carlin, *Inorg. Chem., 14,* 291 (1975).
2 F. J. Hollander, D. H. Templeton and A. Zalkin, *Acta Cryst., B 29,* 1289 (1973).
3 D. Vivien and J. F. Gibson, *J. Chem. Soc. Faraday II,* 1640 (1975).
4 R. B. Birdy and M. Goodgame, *J. Chem. Soc. Dalton,* 461 (1977).
5 A. Chatelain and R. A. Weeks, *J. Chem. Phys., 52,* 3758 (1970).
6 J. F. Baugher, P. C. Taylor, T. Oja and P. J. Bray, *J. Chem. Phys., 50,* 4914 (1969).
7 P. C. Taylor, J. F. Baugher and H. M. Kriz, *Chem. Rev., 75,* 203 (1975).
8 G. C. Upreti, *J. Mag. Res., 18,* 287 (1975).
9 J. N. van Niekerk, F. R. L. Schoening and J. H. Talbot, *Acta Cryst., 6,* 720 (1953).
10 K. Kumagai, K. Ono, I. Hayashi and K. Kambe, *Phys. Rev., 87,* 374 (1952).
11 G. C. Upreti, *J. Mag. Res., 13,* 336 (1974).