Electron Spin Resonance Spectra of Manganese(II) Ions in the Double-stranded Chain Polymers $CdLX_2$ (L = pyridine or methylpyridine; X = Cl or Br)

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E.s.r. spectra at X and Q band are reported for manganese(II) ions doped into $CdLX_2$ (L = pyridine or 3- or 4-methylpyridine; X = Cl or Br). The zero-field splitting parameters D and λ (= E/D) are obtained. For the chlorides D is in the range -0.0576 to -0.0631 cm^{-1}, with $\lambda = 0.04 \pm 0.01$, while for the bromides $|D| = ca.\ 0.185$ cm^{-1}, with $\lambda = 0.07 \pm 0.01$. These figures support the proposed double-stranded polymeric structure, which may readily be identified from the form of the spectrum.

There have been many reports of complexes MLX_2 (L = pyridine or substituted pyridine, X = halide) but evidence concerning their structures is sparse, since the compounds are not so far available as single crystals. They are presumed[1,2] to have octahedral polymeric structures consisting of double-stranded halogen-bridged chains. For non-transition metals, the structural evidence is based on vibrational spectra below 200 cm^{-1}. We report here an e.s.r. study of the cadmium compounds doped with manganese(II) ions, $Cd(Mn)LX_2$ (L = pyridine, 3- or 4-methylpyridine; X = Cl or Br), which confirms the expected structure, provides a criterion for its recognition, and also permits a measurement of the zero-field splitting in this environment.

Results

E.s.r. spectra have been obtained at both X and Q band for manganese(II) ions doped into $CdLX_2$ (L = pyridine, 3- or 4-methylpyridine; X = Cl or Br). The pure manganese compounds give only a strong, broad, symmetrical signal at $g_{\text{eff}} = 2$, as is invariably found for polymeric halide-bridged structures. By contrast, the doped cadmium complexes show a large number of transitions, with, in general, well resolved hyperfine structure (Figures 1—3). The resolution decreases, however, with increasing concentration of manganese, this effect being more noticeable than with the CdL_2X_2 compounds,[3] which have single-chain polymeric structures.

Using first-order perturbation theory, a first estimate was made of $D = ca.\ 0.06$ cm^{-1} for the chloro-complexes, where D is the axial zero-field splitting parameter in the spin Hamiltonian (1). Moreover, it was clear that the D value for the

$$\mathscr{H} = g\beta BS + D(S_z^2 - \tfrac{35}{12}) + E(S_x^2 - S_y^2) \qquad (1)$$

pyridine (py) complex was a little higher than for the methylpyridine complexes and that λ (= E/D) was small but finite. The values were then refined by comparison of the observed resonance-field values at both X and Q band with those calculated using the program[4] ESRS by exact diagonalisation of the matrix derived from equation (1) with $g_{\text{iso}} = 2.00$. The results are shown in Tables 1—4, in which the levels are labelled 1—6 in order of decreasing energy. The calculated single-crystal transition probabilities were all close to the 5:8:9:8:5 ratio predicted from first-order perturbation theory, and are not included in the Tables. The results for the complex of 3-methylpyridine (3Me-py) were very similar to those for that of 4-methylpyridine (4Me-py), a best-fit being obtained with $D = 0.0585$ cm^{-1} and $\lambda = 0.05$.

For all the chloro-complexes the D value was small enough, and the hyperfine splitting sufficiently well resolved, that the sign of D could be determined from the mean spacing of the hyperfine components in the $\pm\frac{3}{2} \leftrightarrow \pm\frac{5}{2}$ transitions, with the magnetic field parallel to z. In each case in the X-band spectra this spacing was greater for the lowest-field allowed transition than for the highest observed band. For example, for $Cd(Mn)(4Me\text{-}py)Cl_2$ the average spacing on the transition at 92 mT was 8.9 mT, compared with 7.9 mT on the band at 584 mT. Assuming that A is negative, D must also be negative.

The X-band spectra of these compounds show weak absorption at about 120—130 mT, assigned as spin-forbidden bands, mainly the $5 \rightarrow 2$ transition in the xz and yz planes. Although these have low single-crystal transition probabilities, they occur at resonance fields which are fairly constant over a range of angles, and hence appear more strongly in the powder spectra. The observed intensity agrees satisfactorily with that in the simulated powder spectrum (Figure 1).

The spectra of the bromides tended to be less well resolved than those of the chlorides, and some samples lost the resolution of hyperfine structure on conversion from $Cd(Mn)L_2Br_2$ into $Cd(Mn)LBr_2$. In all cases the X-band spectra were very complicated, with considerable overlapping of transitions, and detailed interpretation was difficult. However, the strong absorption near zero field suggested a D value of about 0.1—0.2 cm^{-1}. The Q-band spectra showed better resolution (Figure 2) and from these the values of D and λ could be determined with reasonable precision. The results for the pyridine and 4-methylpyridine complexes are shown in Tables 5 and 6. The spectrum of the 3-methylpyridine complex was similar and was fitted with $D = 0.185$ cm^{-1} and $\lambda = 0.08$.

The highest field transition is quite weak in all the compounds, and it is overlaid by the broad oxygen absorption near 2 000 mT. However, weak absorption occurs in this region for both the methylpyridine complexes even after repeated evacuation and flushing with nitrogen, and we believe it to be a genuine feature of the spectra. The D values for the bromides were obtained by fitting the other bands; high-field bands are then predicted near to 2 000 mT.

It was not possible to determine the sign of D for the bromides because of the higher D values. However, it seems likely that it would have the same sign as in the chlorides, and this has been assumed in the Tables. Should D be positive the labels would have to be reversed.

The parameters obtained from the Q-band spectra were then used to simulate the X-band spectra, good agreement being obtained (Figure 3). No assignment of the X-band transitions was possible because the band positions are subject to appreciable uncertainty because of overlapping. However, the low-field bands are seen to arise from transitions between non-

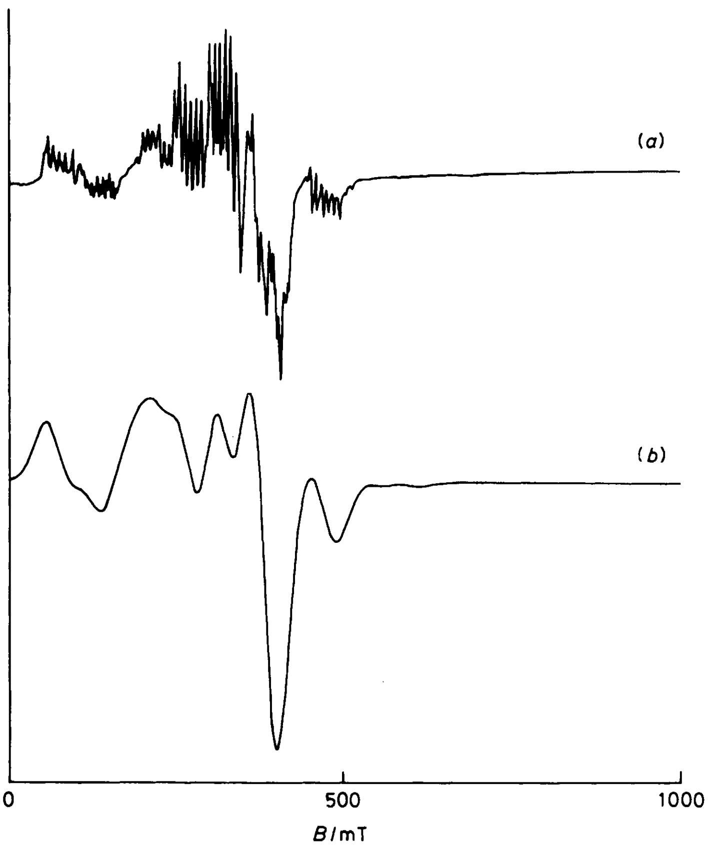

Figure 1. *X*-Band spectrum of $Cd(Mn)(py)Cl_2$: (*a*) experimental; (*b*) simulated with $|D| = 0.0631$ cm^{-1} and $\lambda = 0.03$

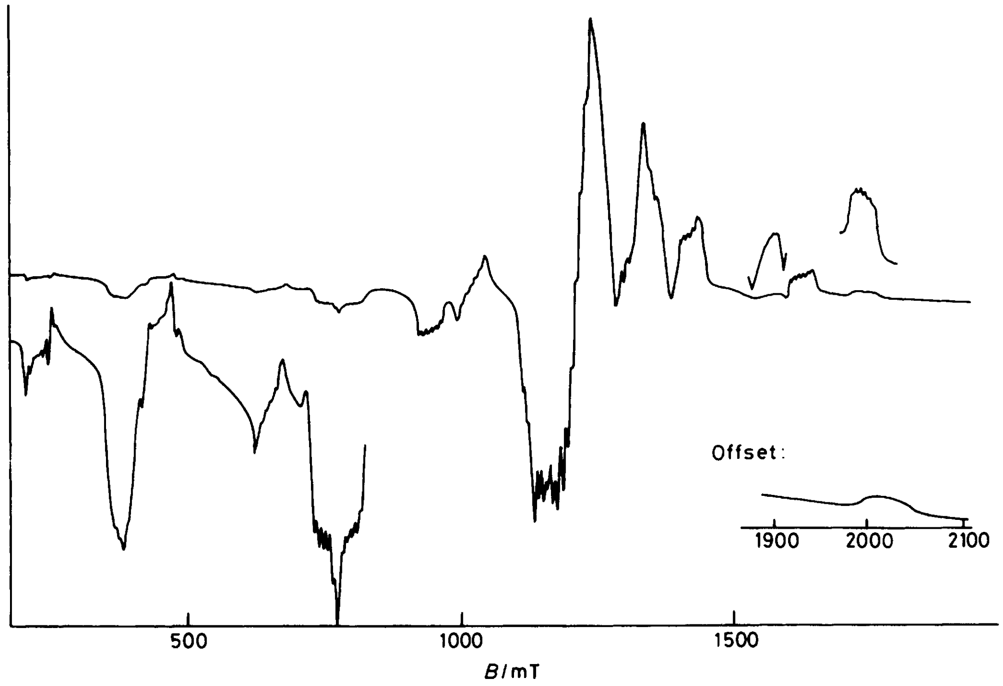

Figure 2. *Q*-Band spectrum of $Cd(Mn)(4Me\text{-}py)Br_2$

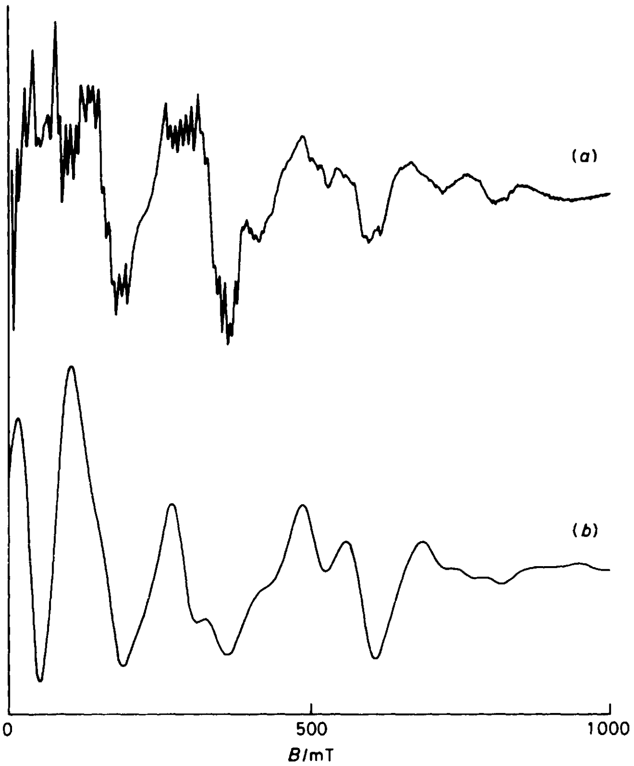

Figure 3. *X*-Band spectrum of Cd(Mn)(4Me-py)Br_2: (*a*) experimental; (*b*) simulated with $|D| = 0.189$ cm^{-1} and $\lambda = 0.07$

Table 1. *X*-Band e.s.r. spectrum (mT) of Cd(Mn)(py)Cl_2

Obs. (ν = 9.470 GHz)	Calc. for $D = -0.0631$ cm^{-1}, $\lambda = 0.03$		
B	*B*	Field direction	Levels
71.1w	67.7	$\theta = 0, \varphi = 50°$	4→1
73.9wm	68.2	*z*	6→5
123.5w	122.0	$\theta = 28, \varphi = 0°$	5→2
128.1w	128.1	$\theta = 33, \varphi = 90°$	5→2
	203.2	*z*	5→4
210.3m	211.5	*y*	2→1
	235.9	*x*	2→1
258.9ms	259.1	*y*	3→2
	267.8	*x*	3→2
307.9s	312.6	*x*	4→3
312.4s	316.7	*y*	4→3
Strong	338.3	*z*	4→3
overlapping	374.2	*x*	5→4
absorption	388.4	*y*	5→4
ca. 320—410			
467.7m	469.6	*x*	6→5
473.5m	473.3	*z*	3→2
493.1w	492.5	*y*	6→5
604.6vw	608.6	*z*	2→1

adjacent levels, which have considerable allowed character at these *D* values.

Discussion

All the compounds were made by heating complexes of stoicheiometry Cd(Mn)L_nX_2 (n = 4 or 2, see Experimental section). The highest complexes obtained were of stoicheiometry CdL_4Br_2 and CdL_2Cl_2 for the bromides and chlorides respectively. This contrasts with previous reports[5] of CdL_6Br_2 and CdL_4Cl_2 prepared in this way.

Table 2. *X*-Band e.s.r. spectrum (mT) of Cd(Mn)(4Me-py)Cl_2

Obs. (ν = 9.481 GHz)	Calc. for $D = -0.0576$ cm^{-1}, $\lambda = 0.045$		
B	*B*	Field direction	Levels
92.4wm	92.3	*z*	6→5
121.9w	121.6	$\theta = 26, \varphi = 0°$	5→2
127.8w	129.5	$\theta = 29, \varphi = 90°$	5→2
216.8w	215.2	*y*	2→1
	215.4	*z*	5→4
244.6m	248.8	*x*	2→1
264.8ms	263.8	*y*	3→2
	276.4	*x*	3→2
315.7s	315.9	*x*	4→3
319.3s	320.8	*y*	4→3
Strong	338.6	*z*	4→3
overlapping	371.0	*x*	5→4
absorption	390.2	*y*	5→4
ca. 330—420			
454.9m	453.1	*x*	6→5
463.0m	461.9	*z*	3→2
481.2w	484.4	*y*	6→5
583.7vw	585.5	*z*	2→1

Table 3. *Q*-Band e.s.r. spectrum (mT) of Cd(Mn)(py)Cl_2

Obs. (ν = 36.18 GHz)	Calc. for $D = -0.0631$ cm^{-1}, $\lambda = 0.03$		
B	*B*	Field direction	Levels
1 024.6vw	1 022.1	*z*	6→5
	1 149.0	*y*	2→1
1 158.4wm	1 157.3	*z*	5→4
	1 173.7	*x*	2→1
1 215.4m	1 215.2	*y*	3→2
1 226.0m	1 226.8	*x*	3→2
1 278.6s	1 285.0	*x*	4→3
	1 285.8	*y*	4→3
1 308.8ms	1 292.4	*z*	4→3
1 349.9m	1 348.7	*x*	5→4
1 361.9m	1 361.4	*y*	5→4
	1 418.7	*x*	6→5
1 434.0w	1 427.6	*z*	3→2
	1 442.6	*y*	6→5
1 564.9vw	1 562.7	*z*	2→1

At the simplest level, the *D* value may be expected to be halved on changing from *trans*-CdN_2X_4 to the $CdNX_5$ chromophore suggested for these compounds, provided the major axis lies along the Cd–N bond direction in each case. This model fits the chloro-complexes surprisingly well, with even the small differences between pyridine and the methylpyridine complexes following the same pattern (Table 7). For the bromides the correspondence is less marked, but even here the *D* values are of the expected order of magnitude. These studies therefore lend support to the proposed structure.

The λ values are somewhat greater than those found for the CdL_2X_2 complexes. In $CdLX_2$ with a double-stranded chain structure, the halide ions are not all equivalent, with half bridging two and half three metal ions. Some rhombicity additional to that due to geometrical distortion might therefore be expected. The λ value is considerably higher for the bromides than for the chlorides, and in both chlorides and bromides is lowest for the pyridine derivative and highest for the 3-methylpyridine, the least symmetrical ligand. The magnitude of

Table 4. Q-Band e.s.r. spectrum (mT) of Cd(Mn)(4Me-py)Cl_2

Obs. (ν = 36.15 GHz)	Calc. for $D = -0.0576$ cm^{-1}, $\lambda = 0.045$		
B	B	Field direction	Levels
1 046.2vw	1 044.7	z	6→5
1 155.6w	1 154.4	y	2→1
1 164.4w	1 168.0	z	5→4
	1 188.2	x	2→1
1 220.5wm	1 218.4	y	3→2
1 233.1wm	1 234.4	x	3→2
	1 284.9	x	4→3
1 286.1s	1 286.0	y	4→3
	1 291.3	z	4→3
1 343.7wm	1 340.3	x	5→4
1 348.7wm	1 357.6	y	5→4
1 406.1wm	1 400.9	x	6→5
	1 414.7	z	3→2
1 432.2w	1 433.7	y	6→5
1 540.4vw	1 538.1	z	2→1

Table 5. Q-Band e.s.r. spectrum (mT) of Cd(Mn)(py)Br_2

Obs. (ν = 33.953 GHz)	Calc. for $D = -0.182$ cm^{-1}, $\lambda = 0.06$		
B	B	Field direction	Levels
250.4vw	253.2	$\theta = 90, \varphi = 67°$	4→1
429.9w	434.5	z	6→5
461.4vw	466.5	$\theta = 24, \varphi = 90°$	5→2
664.7vw	668.2	$\theta = 57, \varphi = 0°$	5→3
731.5vw	733.3	$\theta = 61, \varphi = 90°$	5→3
796.1w	796.7	y	2→1
821.7wm	823.3	z	5→4
933.0m	939.4	x	2→1
969.0m	967.8	y	3→2
1 021.6s	1 023.9	x	3→2
Strong	1 145.7	x	4→3
overlapping	1 163.1	y	4→3
absorption	1 212.3	z	4→3
ca.			
1 120—1 230		x	5→4
1 327.8ms	1 315.1	y	5→4
1 397.6m	1 394.6	x	6→5
1 562.3w	1 556.1	z	3→2
1 601.5wm	1 601.8	y	6→5
1 690.4vw	1 689.2	z	2→1
	1 992.7		

λ suggests that any assumption of localised C_{4v} symmetry in interpreting spectral properties of this type of compound is not really justified.

The negative D found for the chloro-complexes appears to correspond to an octahedron compressed along an approximate four-fold axis. Since the halving of D between CdL_2X_2 and $CdLX_2$ would not be expected if there were a change of sign, we suggest that a negative D may also be appropriate for CdL_2X_2, for which the sign of D was not previously known, and this has been incorporated into Table 7. As implied in this Table, the e.s.r. spectra provide a very easy way of distinguishing between the different stoicheiometries. This can be done merely by considering the general form of each spectrum, without the necessity for detailed analysis and assignment.

Table 6. Q-Band e.s.r. spectrum (mT) of Cd(Mn)(4Me-py)Br_2

Obs. (ν = 33.9 GHz)	Calc. for $D = -0.189$ cm^{-1}, $\lambda = 0.07$		
B	B	Field direction	Levels
255.5vw	249.6	$\theta = 90, \varphi = 61°$	4→1
401.5w	403.4	z	6→5
473.1vw	468.4	$\theta = 27, \varphi = 90°$	5→2
659.3vw	665.0	$\theta = 56, \varphi = 0°$	5→3
763.0w	768.9	y	2→1
805.3wm	806.7	z	5→4
	941.6	x	2→1
949.7m	951.9	y	3→2
1 026.2m	1 018.8	x	3→2
1 135.5s	1 137.1	x	4→3
	1 159.3	y	4→3
1 204.5s	1 210.1	z	4→3
1 314.3ms	1 307.1	x	5→4
1 400.3m	1 404.0	y	5→4
1 544.4vw	1 556.6	x	6→5
1 606.0wm	1 614.5	z	3→2
1 716.9vw	1 717.5	y	6→5
2 021.3vw	2 020.9	z	2→1

Table 7. D and λ values for Cd(Mn)LX_2 and Cd(Mn)L_2X_2

Compound	D/cm^{-1}	λ
Cd(Mn)(py)Cl_2	-0.0631	0.03
Cd(Mn)(3Me-py)Cl_2	-0.0585	0.05
Cd(Mn)(4Me-py)Cl_2	-0.0576	0.045
Cd(Mn)$(py)_2Cl_2$	-0.125	0.02
Cd(Mn)$(4Me\text{-}py)_2Cl_2$	-0.118	0.01
Cd(Mn)(py)Br_2	$(-)$ 0.182*	0.06
Cd(Mn)(3Me-py)Br_2	$(-)$ 0.185*	0.08
Cd(Mn)(4Me-py)Br_2	$(-)$ 0.189*	0.07
Cd(Mn)$(py)_2Br_2$	$(-)$ 0.30*	*ca.* 0

* Negative sign inferred by analogy with chlorides.

Experimental

All the complexes Cd(Mn)LX_2 were made by heating complexes of higher stoicheiometry *in vacuo*. In all cases the observed weight loss agreed with the calculated figure.

Complexes Cd(Mn)L_2Cl_2 were made by dropwise addition of a ten-fold excess of ligand to a stirred solution of Cd(Mn)Cl_2 in hot absolute ethanol containing a few drops of 2,2-dimethoxypropane. Complexes Cd(Mn)L_4Br_2 were made by recrystallisation of Cd(Mn)Br_2 from the pure ligand (*ca.* 15 cm^3) containing *ca.* 2 cm^3 2,2-dimethoxypropane. The complex Cd(Mn)$(py)_4Br_2$ lost ligand on standing at room temperature. After about 1 h it had the stoicheiometry Cd(Mn)$(py)_2Br_2$. The complexes with the methylpyridines were more stable, and could be handled at room temperature without loss of ligand. The compositions of all complexes, before and after thermal decomposition, were confirmed by microanalysis. Doping levels were about 1% in all cases.

X-Band e.s.r. spectra were obtained using a Varian E9 spectrometer, field values for each band being separately measured using a Varian n.m.r. gaussmeter. Q-Band spectra were obtained with a Bruker ER 200D-SRC spectrometer and an ER 078 15-in electromagnet. The field-set and scan range up to 2 000 mT were calibrated using a Bruker gaussmeter. All samples were measured as polycrystalline solids.

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