Zero-field Splitting of Manganese(II) Ions in Polymeric MN_2X_4 (M = Cd or Zn, X = halogen) Co-ordination

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E.s.r. spectra at *X* and *Q* band are reported for manganese(II) ions doped into the halide-bridged polymers $Cd(py)_2X_2$ (X = Cl or Br), $Cd(4Me\text{-}py)_2Cl_2$, $Cd(pyz)X_2$ (X = Cl, Br, or I), and $Zn(pyz)Cl_2\cdot 0.5H_2O$ (py = pyridine, 4Me-py = 4-methylpyridine, pyz = pyrazine). Zero-field splitting parameters *D* and λ (=*E*/*D*) are obtained. For all the complexes λ is close to zero, while *D* is in the range 0.11—0.14 cm^{-1} for the chlorides, and *ca*. 0.3 cm^{-1} for the bromides. The distortion from octahedral geometry is therefore less than in related MnN_4X_2 complexes.

THE e.s.r. spectra of manganese(II) ions in halide-bridged polymeric compounds, such as $Mn(py)_2Cl_2$ (py = pyridine), have been observed invariably to give only strong broad symmetrical lines at $g_{eff.} = 2$. Indeed, where unsymmetrical co-ordination is present, this type of signal is almost diagnostic of such bonding, and has been ascribed to magnetic interactions between neighbouring metal ions. We report here a study of manganese(II) ions doped into some diamagnetic lattices of this type for which well resolved e.s.r. spectra permit estimation of the zero-field splitting parameters of the manganese ions.

RESULTS

E.s.r. spectra have been obtained at both *X* and *Q* bands for manganese(II) ions doped into the polymeric compounds $Cd(py)_2X_2$ (X = Cl or Br), $Cd(4Me\text{-}py)_2Cl_2$, $Cd(pyz)X_2$ (X = Cl, Br, or I), and $Zn(pyz)Cl_2\cdot 0.5H_2O$ (4Me-py = 4-methylpyridine, pyz = pyrazine). Both of the cadmium–pyridine compounds are now known [1] to have polymeric structures similar to that of $Co(py)_2Cl_2$, rather than the asymmetric co-ordination originally postulated. The pure manganese compounds are isomorphous with $Co(py)_2Cl_2$.

In contrast to the pure manganese compounds, most of the polymers, doped with a nominal 1% manganese, show a large number of transitions, with, in general, well defined hyperfine splitting. For several of the complexes, the effect was studied of increasing the nominal doping of manganese. It was found that line-broadening occurred, with collapse of the hyperfine structure, but that the overall appearance of the spectrum remained similar up to at least 20% manganese. Thereafter the spectrum gradually collapsed towards the single $g_{eff.} = 2$ line, thus confirming magnetic concentration as the reason for this type of spectrum.

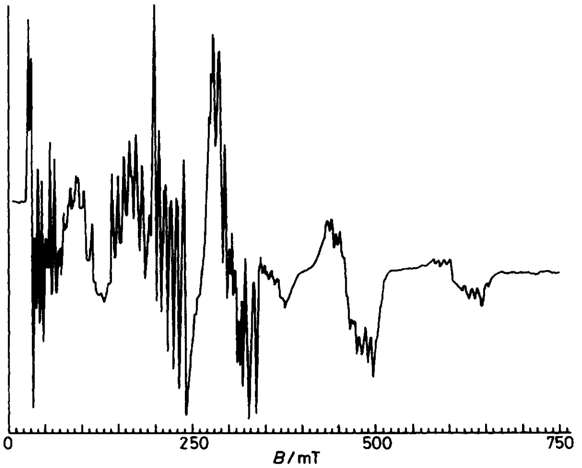

FIGURE 1 Experimental *X*-band spectrum of $(Cd,Mn)(py)_2Cl_2$

At *X* band, all the chlorides containing 1% manganese gave very complicated spectra (Figure 1) with considerable overlapping of transitions. The better resolved *Q*-band spectra were therefore used to calculate the zero-field splitting parameters *D* and λ (= *E*/*D*) in the spin Hamiltonian (1). Experimental resonance fields agreed well with those

$$\mathcal{H} = g\beta B \cdot S + D(S_z^2 - \tfrac{35}{12}) + E(S_x^2 - S_y^2) \quad (1)$$

calculated, using the program [2] ESRS, by exact diagonalisation of the matrix derived from (1) with $g_{iso.} = 2.00$, λ close to zero, and, for the cadmium polymers, *D* in the range 0.11—0.125 cm^{-1}. Details are given in Tables 1—3, where, because of the severe mixing of wavefunctions, levels are labelled 1—6 in decreasing order of energy. In no case have we been able to determine the sign of *D* in these compounds. Assignments are made for positive *D*. Should it be negative, the labels would have to be reversed.

TABLE 1

Q-Band e.s.r. spectrum (mT) of $(Cd,Mn)(py)_2Cl_2$

Obs. (ν = 35.81 GHz)	Calc. for $D = 0.125\ cm^{-1}$, $\lambda = 0.02$			
	B	t.p.*	Field direction	Levels
753m	744.0	5.0	*z*	2→1
1 012ms	1 011.7	8.1	*z*	3→2
	1 013.4	5.1	*y*	6→5
1 047ms	1 016.2	5.1	*x*	6→5
1 124s	1 125.6	8.0	*y*	5→4
1 140s	1 139.9	8.0	*x*	5→4
1 381s	1 383.1	8.0	*x*	3→2
1 398s	1 400.5	8.0	*y*	3→2
1 539ms	1 542.0	5.1	*x*	2→1
1 546ms	1 547.1	8.1	*z*	5→4
1 571ms	1 573.0	5.1	*y*	2→1
1 813w	1 814.9	5.0	*z*	6→5

* t.p. = Single-crystal transition probability.

The parameters obtained from the *Q*-band spectra were then used to simulate the *X*-band spectra, using the program [3] SHAPE 9. The agreement with experiment was good. Some assignment of the transitions was also possible (Table 4), although the observed band positions are subject to appreciable uncertainty because of overlapping.

The complexes ZnL_2X_2, where L is pyridine or methylpyridine, have tetrahedral monomeric structures. How-

TABLE 2

Q-Band e.s.r. spectrum (mT) of (Cd,Mn)(4Me-py)$_2$Cl$_2$

Obs. (ν = 35.86 GHz)	Calc. for D = 0.118 cm^{-1}, λ = 0.01			
	B	t.p.	Field direction	Levels
461w	464.0	0.1	$\theta = 30°, \phi = 0°$	5→2
	466.0	0.1	$\theta = 30°, \phi = 90°$	5→2
683w	686.0	0.5	$\theta = 60°, \phi = 0°$	4→2
	692.0	0.5	$\theta = 60°, \phi = 90°$	4→2
773m	775.5	5.0	z	2→1
1 036ms	1 036.5	5.1	y	6→5
1 053ms	1 052.0	5.1	x	6→5
1 138s	1 139.6	8.0	y	5→4
1 146s	1 146.4	8.0	x	5→4
1 381s	1 384.3	8.0	x	3→2
1 390s	1 392.5	8.0	y	3→2
1 531ms	1 533.7	8.0	z	5→4
	1 535.8	5.1	x	2→1
1 549ms	1 546.8	5.1	y	2→1
1 787w	1 786.5	5.0	z	6→5

TABLE 3

Q-Band e.s.r. spectrum (mT) of (Cd,Mn)(pyz)Cl$_2$

Obs. (ν = 35.735 GHz)	Calc. for D = 0.111 cm^{-1}, λ = 0.01			
	B	t.p.	Field direction	Levels
456w	459.3	0.1	$\theta = 30°, \phi = 0°$	5→2
	461.6	0.1	$\theta = 30°, \phi = 90°$	5→2
681w	679.4	0.4	$\theta = 60°, \phi = 0°$	4→2
	684.9	0.5	$\theta = 60°, \phi = 90°$	4→2
800vw	801.1	5.0	z	2→1
1 000—1 080m	1 038.8	8.0	z	3→2
	1 045.5	5.1	y	6→5
	1 060.1	5.1	x	6→5
1 141s	1 143.9	8.0	y	5→4
1 150s	1 150.4	8.0	x	5→4
1 371s	1 374.9	8.0	x	3→2
1 380s	1 382.6	8.0	y	3→2
1 514m	1 514.3	8.0	z	5→4
	1 515.9	5.1	x	2→1
1 531m	1 529.7	5.1	y	2→1
vw Absorption centred on 1 750	1 752.0	5.0	z	6→5

TABLE 4

X-Band e.s.r. spectrum (mT) of (Cd,Mn)(py)$_2$Cl$_2$

Obs. [a] (ν = 9.53 GHz)	Calc. for D = 0.125 cm^{-1}, λ = 0.02			
	B	t.p.	Assignment	
0—50ms [b]	36	3.29	x	3→6
	37	4.13	y	4→6
70m	71	12.4	z	3→5
148m	149	9.07	y	5→6
ca. 170m	175	9.30	x	5→6
210s [b]	197	7.75	z	3→5
	204	12.0	y	4→5
	207	11.9	x	4→5
270—340s [b]	295	11.2	x	3→4
	309	11.2	y	3→4
	339	14.0	z	3→5
260—480m [c]			Off axis, mainly yz	
605	607	12.6	z	4→5
	610	8.92	x	1→2
636	639	8.82	y	1→2
	875	7.86	z	5→6

[a] Also weak z transitions predicted at 114, 153, and 382 mT. [b] At least two overlapping transitions. [c] Broad poorly resolved.

ever, Zn(pyz)Cl$_2$ is considered, on i.r. spectral evidence,[4] to be octahedral, with bridging pyrazine and chloride ions. The e.s.r. spectrum of the manganese-doped complex supports this conclusion, although our compounds always analysed as Zn(pyz)Cl$_2$·0.5H$_2$O, and i.r. spectra confirmed the presence of water.

At both *X* and *Q* bands, the e.s.r. spectra are similar to those of Cd(py)$_2$Cl$_2$, but are interpreted with the somewhat higher *D* value of 0.143 cm^{-1} (Table 5).

TABLE 5

Q-Band e.s.r. spectrum (mT) of (Zn,Mn)(pyz)Cl$_2$·0.5H$_2$O

Obs. (ν = 35.820 GHz)	Calc. for D = 0.143 cm^{-1}, λ = 0.03			
	B	t.p.	Field direction	Levels
696w	667.1	5.0	z	2→1
	969.6	5.1	y	6→5
970m	973.3	8.0	z	3→2
1 022m	1 026.0	5.1	x	6→5
1 098s	1 098.7	8.0	y	5→4
1 126s	1 122.7	8.0	x	5→4
1 395s	1 388.7	8.0	x	3→2
1 417s	1 418.9	8.0	y	3→2
1 567m	1 572.4	5.1	x	2→1
	1 585.7	8.0	x	5→4
1 624m	1 625.3	5.1	y	2→1
	1 892.1	5.0	z	6→5

The compound (Cd,Mn)(py)$_2$Br$_2$ gives an *X*-band spectrum with its strongest band near 120 mT ($g_{\text{eff.}}$ = 6), and a number of bands to higher field. This is typical of axial or near-axial species with *D* in the range 0.20—0.55 cm^{-1}. The value of *D* was determined as 0.30 cm^{-1} from the *Q*-band spectrum (Table 6).

TABLE 6

Q-Band e.s.r. spectrum (mT) of (Cd,Mn)(py)$_2$Br$_2$

Obs. (ν = 35.840 GHz)	Calc. for D = 0.30 cm^{-1}, λ = 0			
	B	t.p.	Field direction	Levels
231m	230.7	0.5	$\theta = 65°$	6→3
460m	464.3	2.0	$\theta = 35°$	5→2
643w	637.0	7.9	z	3→2
700—800m	766.9	5.5	y, x	6→5
	807.0	2.3	$\theta = 55°$	4→2
928s	931.2	7.9	y, x	5→4
1 153vs	1 156.5	8.3	y, x	4→3
1 280w	1 280.2	8.9	z	4→3
1 439m	1 438.0	7.5	y, x	3→2
ca. 1 525m *	1 527.9	7.4	$\theta = 35°$	4→3
	1 541.8	7.0	$\theta = 70°$	3→2
1 941w	1 922.8	7.9	z	5→4
	1 961.9	5.3	y, x	2→1

* Hyperfine structure absent.

Simulation of the *X*-band spectrum with D = 0.30 cm^{-1} and λ = 0 gives good agreement with the experimental trace (Figure 2), but only three of the observed bands are due to along-axis transitions (Table 7) and these are all in the *x*, *y* direction. The only two *z* transitions predicted below 1 200 mT are intrinsically weaker, and may well be hidden in the absorption at *ca.* 1 000 mT. The other, mostly weak, bands are due to transitions within the *xz* and *yz* planes, the intensity of which is a function not only of the transition probability at the turning point, but also of the orientation of the magnetic field and the rate of bending at the turning point. For example, the band at *ca.* 725 mT for (Cd,Mn)(py)$_2$Br$_2$, which appears relatively strongly in the experimental trace, may be assigned to the 3→2 transition in the *xz* and *yz* planes, which reaches a maximum of both transition probability and field value (736 mT) when $\theta = 61°$. The wavefunctions are very mixed, but this is predominantly a $+\frac{1}{2}\rightarrow+\frac{3}{2}$ transition.

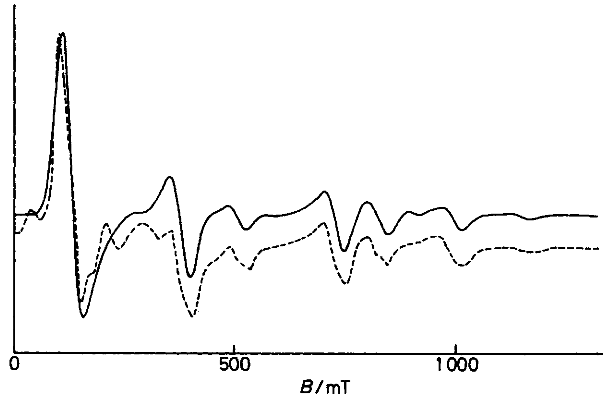

FIGURE 2 Experimental *X*-band spectrum (– – –) of (Cd,Mn)-$(py)_2Br_2$ with a nominal doping of 20% and calculated spectrum (——) for $D = 0.30$ cm^{-1}, $\lambda = 0$

The compound (Cd,Mn)(pyz)Br_2 gives spectra at *X* and *Q* bands very similar to those of (Cd,Mn)$(py)_2Br_2$, confirming the suggested [5] polymeric structure. The spectra may be fitted with $D = 0.31$ cm^{-1} and $\lambda = 0$.

The corresponding zinc complex, Zn(pyz)Br_2, is thought to have a tetrahedral structure [4] like Zn$(py)_2Br_2$. A similar structure has been suggested for Cd$(py)_2I_2$ on the basis of vibrational spectra.[5] Attempts to prepare manganese-doped samples of these complexes were unsuccessful, probably because of the quite different structure of the manganese compounds. Most attempts at preparation resulted in samples with reasonably good analyses, but with e.s.r. spectra showing only a weak but well resolved sextet at $g_{eff.} = 2$. We believe that this originates from traces of the manganese-doped metal halides MX_2 present as impurities.

TABLE 7

X-Band e.s.r. spectrum (mT) of (Cd,Mn)$(py)_2Br_2$

Obs.	Calc. for $D = 0.30$ cm^{-1}, $\lambda = 0$		
(ν = 9.531 GHz)	*B*	Field direction	Levels
ca. 35vw			
ca. 120s	121	*x*, *y*	6→5
175 (sh)			
235w,br			
325w			
390m	388	*x*, *y*	4→3
510w	517	$\theta = 14°$	5→4
720 (sh)			
740m	736	$\theta = 61°$	3→2
ca. 800			
ca. 825	831	$\theta = 26°$	4→3
	945	*z*	
	982	*z*	
ca. 1 000mw	1 003	*x*, *y*	2→1
1 150	1 157	$\theta = 7°$	5→4

In contrast to this, the *X*-band spectrum of (Cd,Mn)-(pyz)I_2 shows a strong unsplit $g_{eff.} = 6$ band, and a weaker band at *ca.* 820 mT. The extreme simplicity of the spectrum suggests a high axial zero-field splitting, and assignment of the high-field band as *x*, *y* (4→3) gives $D = 1.23$ cm^{-1}, $\lambda = ca.\ 0$. The *Q*-band spectrum shows the three fine-structure lines predicted for these parameters, but several other transitions are also observed over the whole field range, and no satisfactory fit was achieved. However, the clear difference of this compound from the tetrahedral species tends to confirm the suggested [5] octahedral structure.

Attempts were also made to prepare the corresponding manganese-doped complexes of mercury, for which the known unsymmetrical halide co-ordination would be expected to result in larger values of λ. In all cases, however, either the doping was unsuccessful or the e.s.r. spectra produced were of poor quality and did not warrant analysis.

DISCUSSION

The zero-field splitting parameters for the polymers are summarised in Table 8, together with values for some MN_4X_2 complexes. In all the polymers λ is very small, although the true site symmetry of the metal ion must be lower than D_{4h}. This result is significant because it justifies the commonly made assumption of D_{4h} symmetry for the interpretation of spectral and magnetic data for these complexes.

TABLE 8

Zero-field splitting (z.f.s.) parameters of Mn^{II} in some polymeric complexes

Complex	Z.f.s. parameters	
	D/cm^{-1}	λ
(*i*) MN_2X_4		
Cd$(py)_2Cl_2$	0.125	0.02
Cd(4Me-py)$_2Cl_2$	0.118	0.01
Cd$(py)_2Br_2$	0.30	0
Zn(pyz)$Cl_2\cdot0.5H_2O$	0.143	0.03
Cd(pyz)Cl_2	0.111	0.01
Cd(pyz)Br_2	0.31	0
(*ii*) MN_4X_2		
Zn$(N_2H_4)_2Cl_2$	0.29	0.015 *
Cd$(N_2H_4)_2Cl_2$	0.24	0.015 *
Zn$(N_2H_4)_2Br_2$	0.71	0 *
Cd$(N_2H_4)_2Br_2$	0.67	0.006 *

* From ref. 6.

Comparison of the *D* values for (Cd,Mn)$(py)_2X_2$ and (Cd,Mn)(pyz)X_2 confirms the roughly equal ligand-field strengths of pyridine and bridging pyrazine. A more unexpected result is the very large difference in the values of *D* for the donor sets *trans*-N_4X_2 and -N_2X_4. The apparently lower axial distortion in the latter might be rationalised on the assumption that the principal *D*-tensor axis lies along the unique metal–ligand axis in MN_4X_2, but in the plane of the halide ions in the polymers. However, this should lead to a significant rhombic distortion in the polymers, which is not observed.

Both the Co–N and Co–Cl lengths in Co$(py)_2Cl_2$ exceed those in Co$(py)_4Cl_2$ by *ca.* 0.2 Å; if this is generally true for the species MN_2X_4 and MN_4X_2, somewhat lower *D* values for the former would be expected on electrostatic grounds. A similar situation arises when the host metal ion is changed from zinc to cadmium, where the difference in ionic radii is also *ca.* 0.2 Å. It is observed here in the difference between the compounds M(pyz)Cl_2, where M = Zn or Cd, and has been reported in other systems.[6]

This difference, however, is much smaller than that between the N_2X_4 and N_4X_2 donor sets, and some additional explanation of the latter seems called for. It is instructive in this respect to compare the e.s.r. results with the reported crystal-field parameters for $Ni(py)_2X_2$.[7]

Two different assignments have been reported for the electronic bands of $Ni(py)_2X_2$ (X = Cl or Br). That which is said[7] to give the better agreement between experimental and calculated band positions requires the distortion from octahedral symmetry, as measured by $\Delta_{xy} - \Delta_z$, to be less than that in $Ni(py)_4X_2$, in agreement with the measured values of D for the manganese compounds. The explanation proposed is the reduction in π-donor capacity of the halide ions when they act as bridging ligands.

EXPERIMENTAL

Preparation of Complexes.—(Cd,Mn)$(py)_2Cl_2$. This compound was obtained on dropwise addition of a large excess of pyridine to a hot suspension of powdered $CdCl_2 \cdot 2.5H_2O$ and $MnCl_2 \cdot 4H_2O$ in equal volumes of ethanol and 2,2-dimethoxypropane. The precipitated solid was stirred under nitrogen for several minutes. The 4-methylpyridine complex was prepared similarly.

(Cd,Mn)$(py)_2Br_2$. This compound was obtained on dropwise addition of a hot ethanol solution of $CdBr_2 \cdot 4H_2O$ and $MnBr_2 \cdot 4H_2O$ to a 10-fold excess of pyridine in ethanol.

(Zn,Mn)(pyz)$Cl_2 \cdot 0.5H_2O$. An acetone solution of pyrazine was added dropwise to a vigorously stirred suspension of $ZnCl_2$ and $MnCl_2 \cdot 4H_2O$ in the same solvent, the metal–ligand ratio being 5 : 1. The finely divided product was stirred for several minutes, washed with ethanol to remove unreacted $ZnCl_2$, and air-dried.

(Cd,Mn)(pyz)X_2 (X = Cl *or* Br). The appropriate cadmium and manganese halides in boiling ethanol were added to an ethanol solution containing two equivalents of pyrazine.

Analyses for C, H, and N (Microanalytical Laboratory, Imperial College) were in agreement with the above formulae. E.s.r. spectra were obtained as described previously,[2] using polycrystalline samples at room temperature.

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