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Steric and Electronic Effects in Complexes of Cadmium Halides with Substituted Pyridines

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Abstract

ESR spectra at X- and Q-band frequencies are reported for manganese(II) ions doped into the halide-bridged polymeric complexes CdL_2X_2 (L = pyridine or substituted pyridine, X = Cl or Br). Zero-field splitting parameters D and λ ($=E/D$) are obtained. The D values, which give a measure of axial distortion, are influenced by both steric and electronic factors. In general, D values are high when the pyridine ligand is a good σ-donor, and low when it is a poor σ-donor, while steric hindrance by the substituent reduces the D value. Values of λ depend on the position of the substituent. The similarity of Cd(4-hydroxypyridine)$_2$Cl$_2$ to the other complexes suggests that it is N-bonded.

Introduction

We have previously shown that whereas the ESR spectra of halide-bridged complexes such as Mn-pyridine$_2$Cl$_2$ invariably give only broad signals at $g_{eff} = 2$, good and informative spectra may be obtained by dilution in the similar cadmium complexes [1]. The resolution of the spectra is such that zero-field splittings, and hence an estimate of the distortion from true octahedral symmetry, can be obtained to a considerable degree of accuracy. We have now used the ESR spectra of the complexes Cd(Mn)L_2X_2 (L = substituted pyridine, X = Cl or Br) to study differences in the bonding for a series of substituents in the pyridine ring. These studies are limited to substituents in the 3- and 4-positions, since 2-substituted pyridines tend to form tetrahedral CdL_2X_2, which do not dope well with manganese.

Results

ESR spectra at both X- and Q-band frequencies have been obtained for the compounds Cd(Mn)L_2X_2 (L = pyridine and 4-methyl- and 3,5-dimethyl pyridines, X = Cl or Br), Cd(Mn)L_2Cl_2 (L = 3- and 4-cyano-, 3-chloro-, 3-bromo-, 3-methyl-, 3,5-dichloro-, and 3- and 4-hydroxy-pyridine) and Cd(Mn)L_2Br_2 (L = 3,4-dimethylpyridine).

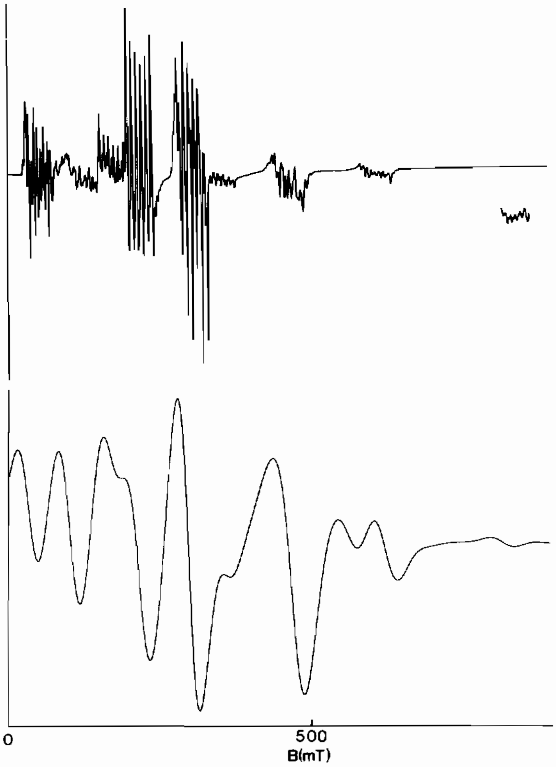

Fig. 1. X-band ESR spectrum of Cd(Mn)(3,5-DiMepy)$_2$Cl$_2$ and simulated spectrum for $|D|$ = 0.120 cm^{-1}, λ = 0.01.

All the chlorides gave extremely complicated spectra at X-band, with considerable overlapping of transitions, and high intensity near zero-field, near 200 mT and in the g_{eff} = 2 region (Fig. 1). The general similarity to Cd(Mn)pyridine$_2$Cl$_2$ was clear, though the details of the spectra varied from one compound to another. The Q-band spectra showed much better resolution (Fig. 2) and were used to calculate the zero-field splitting parameters D and λ($=E/D$) in the spin Hamiltonian (1).

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$$\mathcal{H} = g\beta B \quad S + D(S_{z^2} - 35/12) + E(S_{x^2} - S_{y^2}) \qquad (1)$$

The program ESRS [2] was used to calculate the resonance fields by exact diagonalisation of the matrix derived from (1). Good agreement with the experimental resonance fields was found with g_{iso} = 2.00, D in the range 0.10 to 0.13 cm^{-1}, and λ small but finite. Details for several of the compounds are given in Tables I–III, where the levels are labelled 1–6 in order of decreasing energy, because wavefunctions in the x and y directions are considerably mixed. In no case have we been able to determine the sign of D in these compounds because of the severe overlapping of transitions at X-band. However, since D is negative for Cd(Mn)pyridineCl$_2$, and because it seems likely [3] that Cd(Mn)pyridine$_2$Cl$_2$ would have the same sign, we have assumed a negative D in these Tables. Should D be positive, the labels would have to be reversed.

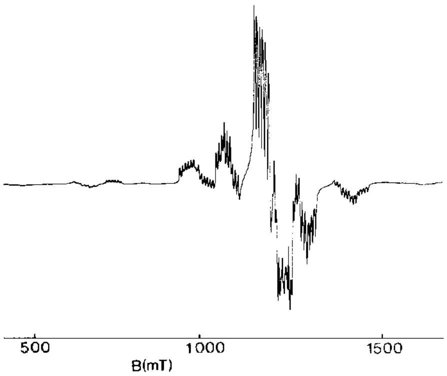

Fig. 2. Q-band ESR spectrum of Cd(Mn)(3-Brpy)$_2$Cl$_2$.

TABLE I. Q-Band ESR Spectrum (mT) of Cd(Mn)(3-OHpy)$_2$-Cl$_2$.

Obs. (ν = 34.003 GHz)	Calc. for D = –0.130, λ = 0.01		
	B	Field Direction	Levels
273.2 vw	274.5	y	4 → 1
277.1 vw	277.5	x	4 → 1
451.4 w	451.0	θ = 14°, ϕ = 90°	5 → 2
507.2 vw			
658.4 w	657.7	z	6 → 5
674.0 w	661.9	θ = 61°, ϕ = 0°	5 → 3
	669.0	θ = 62°, ϕ = 90°	5 → 3
933.7 m	936.1	z	5 → 4
942.4 m	948.7	y	2 → 1
967.5 m	965.8	x	2 → 1
1056.5 m	1057.7	y	3 → 2
1066.2 m	1065.1	x	3 → 2
1190.5 s	1182.9	x	4 → 3
	1184.3	y	4 → 3
1214.4 ms	1214.5	z	4 → 3
1323.2 m	1324.3	x	5 → 4
1336.6 m	1333.4	y	5 → 4
1486.7 wm	1493.0	z	3 → 2
	1496.5	x	6 → 5
1510.3 wm	1512.5	y	6 → 5
1772.5 vw	1771.4	z	2 → 1

TABLE II. Q-Band ESR Spectrum (mT) of Cd(Mn)(4-CNpy)$_2$Cl$_2$.

Obs. (ν = 34.001 GHz	Calc. for D = –0.115 cm^{-1}, λ = 0.015		
	B	Field Direction	Levels
441.3 vw	441.0	θ = 21°, ϕ = 0°	5 → 2
444.5 vw	444.4	θ = 22°, ϕ = 90°	5 → 2
502.1 vw			
Overlapping signals 643 to 669 w	651.2	θ = 62°, ϕ = 0°	5 → 3
	660.2	θ = 63°, ϕ = 90°	5 → 3
Overlapping region 710–760 w	722.0	z	6 → 5
	740.2	θ = 16°, ϕ = 0°	4 → 2
	742.2	θ = 17°, ϕ = 90°	4 → 2
967.0 m	968.3	z	5 → 4
	973.0	y	2 → 1
996.0 m	995.7	x	2 → 1
1073.2 m	1074.9	y	3 → 2
1084.7 m	1084.9	x	3 → 2
Overlapping signals 1189.7 to 1312.6 s/ms	1189.4	x	4 → 3
	1191.0	y	4 → 3
	1214.6	z	4 → 3
	1312.7	x	5 → 4
1327.7 m	1324.7	y	5 → 4
1459 wm	1459.5	x	6 → 5
	1460.9	z	3 → 2
1488.1 wm	1481.0	y	6 → 5
	1707.2	z	2 → 1

The parameters obtained from the Q-band spectra were then used to simulate the X-band spectra using the program SHAPE 9 [4]. The agreement with experiment was good (Fig. 1). In particular, the position of the highest field band (2 → 1 in the z direction) which is an almost pure +3/2 → +5/2 transition, tended to confirm the relative values of D deduced from the Q-band spectra.

More difficulty was experienced in obtaining good spectra for the bromides. With most of the ligands used, the doping was poor, and spectra with broad, poorly defined bands were obtained, even at low nominal doping levels. Good, well-resolved spectra were obtained only for pyridine and methyl-substituted pyridines. For the pyridine complex, the spectra were in good agreement with those published previously [1], allowance being made for the difference in microwave frequency. However, at Q-band

TABLE III. Q-Band ESR Spectrum (mT) of Cd(Mn)(3-CNpy)$_2$Cl$_2$.

Obs. (ν = 33.934 GHz)	Calc. for $D = -0.1032$ cm^{-1}, $\lambda = 0.02$		
	B	Field Direction	Levels
286.4 vw	287.8	$\theta = 90°, \phi = 80°$	4 → 1
354 vw	353.2	x	5 → 2
358 vw	357.2	y	5 → 2
434.5 w	434.3	$\theta = 30°, \phi = 0°$	5 → 2
438.0 w	438.4	$\theta = 30°, \phi = 90°$	5 → 2
647.2 w	642.2	$\theta = 64°, \phi = 0°$	5 → 3
		$\theta = 63°, \phi = 90°$	5 → 3
721.0 w	722.4	$\theta = 15°, \phi = 0°$	4 → 2
	724.3	$\theta = 16°, \phi = 90°$	4 → 2
770.7 w	770.1	z	6 → 5
987.9 wm	990.3	y	2 → 1
	991.2	z	5 → 4
1017.0 wm	1017.4	x	2 → 1
1085.6 m	1086.0	y	3 → 2
1097.9 m	1098.0	x	3 → 2
Overlapping signals 1192.0 to 1300.3 s/ms	1191.6	x	4 → 3
	1193.3	y	4 → 3
	1212.2	z	4 → 3
	1300.5	x	5 → 4
1315.3 m	1314.7	y	5 → 4
1429.0 wm	1428.2	x	6 → 5
	1433.2	z	3 → 2
1456.2 wm	1453.9	y	6 → 5
1654.0 vw	1654.3	z	2 → 1

TABLE IV. Q-Band ESR Spectrum (mT) of Cd(Mn)(4-Mepy)$_2$Br$_2$.

Obs. (ν = 33.983 GHz)	Calc. for $D = -0.291$ cm^{-1}, $\lambda = 0.02$		
	B	Field Direction	Levels
31.9 s	31.6	z	5 → 3
	100.0	x	5 → 4
	150.0	y	6 → 4
222.2 wm	220.8	x	4 → 1
	222.9	y	4 → 1
Overlapping signals 428 to 456 wm	403.2	z	5 → 2
	427.3	$\theta = 33°, \phi = 0°$	5 → 2
591.3 w	591.5	z	5 → 3
700.5 m	683.4	y	2 → 1
776 wm	755.6	x	2 → 1
Overlapping signals 845 to 890 ms	865.6	y	3 → 2
	886.8	x	3 → 2
1081.2 s	1084.2	x	4 → 3
1097.2 s	1102.7	y	4 → 3
1213.0 w	1214.1	z	4 → 3
1335.6 m	1337.7	x	5 → 4
1386.3 m	1384.5	y	5 → 4
Overlapping signals 1440–1500 ms	1445.9	$\theta = 70°, \phi = 0°$	5 → 4
	1448.4	$\theta = 37°, \phi = 0°$	4 → 3
	1493.3	$\theta = 71°, \phi = 90°$	5 → 4
1843.9 wm	1836.9	z	3 → 2
	1840.8	x	6 → 5
1910.6 w	1910.1	y	6 → 5

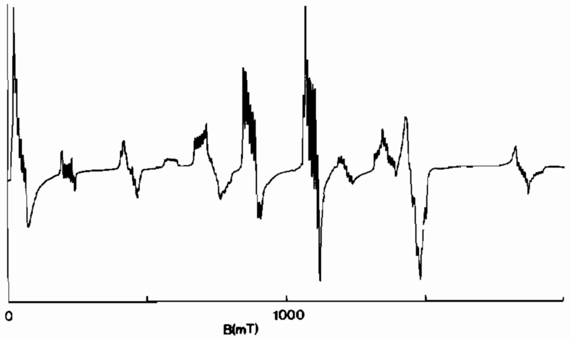

Fig. 3. Q-band ESR spectrum of Cd(Mn)(3,5-DiMepy)$_2$Br$_2$.

we have observed the lowest field band, not previously seen for instrumental reasons, which is important to an accurate assessment of D (Fig. 3).

This band, due to the ±3/2 → ±5/2 transition, is at zero field when $h\nu = 4D$, but moves rapidly upfield at D values both above and below this. For a particular position of the band, therefore, two values of D may be found to correspond with it. The choice between these rests on the remainder of the spectrum. In all the bromides we were able to study, a good fit for all the bands was obtained with the higher of the two possible D values (Table IV). The sensitivity of this lowest band permitted a more accurate assessment of D for Cd(Mn)pyridine$_2$Br$_2$ than was previously possible, and also showed clearly the differences between the ligands.

The D values obtained were used to simulate the X-band spectra, and gave good agreement with experiment (Fig. 4). No attempt has been made to carry out detailed assignments at X-band, because of the overlapping of transitions, and the fact that many of the observed bands are due to 'off-axis' transitions.

Discussion

Values of D and λ for all the complexes are collected in Table V. All the λ values are fairly small, in line with the approximate D_{4h} symmetry often assumed for complexes of this type. The λ values for the 3-substituted pyridines, however, are in general higher than for the other compounds, suggesting that some asymmetry in the xy plane is introduced here.

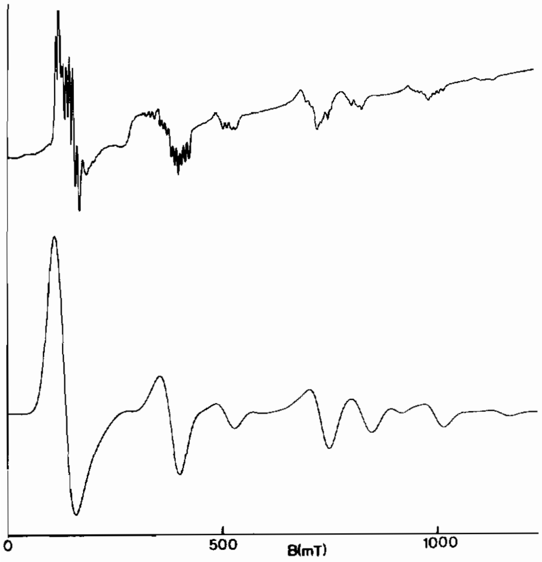

Fig. 4. X-band ESR spectrum of Cd(Mn)(3,4-DiMepy)$_2$Br$_2$ and simulated spectrum for $|D|$ = 0.293 cm^{-1}, λ = 0.015.

TABLE V. Zero Field Splitting Parameters for the Complexes.

L	D (cm^{-1})	λ	pK_a [5]
Cd(Mn)L$_2$Cl$_2$			
Pyridine	−0.125	0.02	5.17
3-Mepyridine	−0.115	0.03	5.68
4-Mepyridine	−0.118	0.01	6.02
3,5-Me$_2$pyridine	−0.120	0.01	6.15
3-CNpyridine	−0.1032	0.02	1.45
3-Clpyridine	−0.1126	0.03	2.84
3-Brpyridine	−0.111	0.04	2.84
3-OHpyridine	−0.130	0.01	4.86
4-CNpyridine	−0.115	0.015	1.90
4-OHpyridine	−0.125	0.05	
3,5-Cl$_2$pyridine	−0.113	0.015	
Cd(Mn)L$_2$Br$_2$			
Pyridine	−0.299	0.005	5.17
4-Mepyridine	−0.291	0.02	6.02
3,4-Me$_2$pyridine	−0.293	0.015	6.46
3,5-Me$_2$pyridine	−0.294	0.02	6.15

The effect does not occur with the bromides, and is probably due to a steric interaction which is relieved with longer metal–metal distances. In this connection it is interesting that we have been unable to prepare complexes CdL$_2$Cl$_2$ with 3,4-disubstituted pyridines, but always obtained CdLCl$_2$, whereas with cadmium bromide 3,4-dimethyl-pyridine gave a complex CdL$_2$Br$_2$.

Nearly all the ligands gave a smaller distortion from octahedral symmetry, as measured by D, than did pyridine, even though several of them have higher pK_a values, and are presumably better sigma donors. Again the most likely explanation lies in the steric requirements of the ligands, which presumably in some cases force a lengthening of the metal–nitrogen bonds. The alternative lengthening of the metal–halide bonds, which would produce larger D values, seems not to be adopted, at least for the chlorides. Indeed, there is a very strong tendency in all these compounds for the chloride-bridged structure to be adopted, and Cd–Cl bonding seems very strong.

For a particular position of substitution, however, there is a general correlation between D value and pK_a for the ligand, with electron-withdrawing substituents giving low D values and electron-releasing ones high D values. There is no real evidence for occurrence of π-back-bonding, which would be expected to increase the D-values, particularly perhaps in the cyano-complexes. However, the greater distortion of Cd(Mn)4-cyanopyridine$_2$Cl$_2$ compared with the 3-cyanopyridine analogue may be evidence for some π-bonding contribution.

The ligand 4-hydroxypyridine, which exists largely in the pyridone tautomeric form, reacts with cadmium chloride in a very similar way to the other ligands studied. The infrared spectrum of the complex shows a number of changes compared with the free ligand, particularly in the appearance of strong bands at 1580 and 730 cm^{-1}, and the disappearance of bands at 1030 and 960 cm^{-1}. Some less well-defined changes occur in the 3000–3400 cm^{-1} region. However, in the absence of detailed band assignments, and because of the considerable coupling of modes in compounds of this type, we are unable to distinguish in this way between O- and N-bonded forms.

The ESR spectra provide much more definite evidence. They are very similar in form to those of the other chlorides (Table VI), and the D value found is towards the high end of the range observed in these compounds. This marks 4-hydroxypyridine as either one of the strongest σ-donors of the group, or else a strong π-acceptor. Neither of these is consistent with donation from a keto-group, and the ESR evidence suggests strongly that the complex is N-bonded, like all the other compounds studied.

Experimental

Preparation of Compounds

Commercial reagent grade materials were used throughout without further purification. In all cases sufficient MnX$_2$·nH$_2$O was used to give a nominal doping of 1 mol%, and 2,2-dimethoxypropane was added to remove water.

Cd(Mn)L$_2$Cl$_2$

CdCl$_2$·2½H$_2$O and MnCl$_2$·4H$_2$O were dissolved in absolute ethanol with warming. To this solution was

TABLE VI. Q-Band ESR Spectrum (mT) of Cd(Mn)(4-OHpy)$_2$Cl$_2$.

Obs. (ν = 34.001 GHz)	Calc. for $D = -0.125$ cm^{-1}, $\lambda = 0.05$		
	B	Field Direction	Levels
Overlapping signals 647–679 vw	645.3	$\theta = 63°, \phi = 90°$	$5 \rightarrow 3$
	678.9	$\theta = 61°, \phi = 0°$	$5 \rightarrow 3$
	679.4	z	$6 \rightarrow 5$
924.9 w	925.1	y	$2 \rightarrow 1$
945.9 w	946.8	z	$5 \rightarrow 4$
1005.5 wm	1007.2	x	$2 \rightarrow 1$
1050.5 wm	1049.7	y	$3 \rightarrow 2$
1085.1 wm	1085.2	x	$3 \rightarrow 2$
1155.0 m			
1183.5 m	1182.7	x	$4 \rightarrow 3$
Overlapping signals 1189 to 1349.0 s/ms	1189.0	y	$4 \rightarrow 3$
	1214.3	z	$4 \rightarrow 3$
	1303.7	x	$5 \rightarrow 4$
	1347.4	y	$5 \rightarrow 4$
1458.0 wm	1454.5	x	$6 \rightarrow 5$
1484.5 wm	1482.0	z	$3 \rightarrow 2$
1533.7 wm	1531.8	y	$6 \rightarrow 5$
1750.5 vw	1750.1	z	$2 \rightarrow 1$

added, with stirring, a solution of the pyridine ligand in the same solvent, using a slight excess over the 2:1 mol ratio required. The precipitated products were filtered off and dried. Use of a larger excess of ligand gave the same products.

Cd(Mn)L$_2$Br$_2$

CdBr$_2$·4H$_2$O and MnBr$_2$·4H$_2$O were recrystallised from the appropriate ligand. In all cases the initial product was Cd(Mn)L$_4$Br$_2$, but for L = pyridine the complex decomposed under ambient conditions, losing 2 mol of ligand to form Cd(Mn)L$_2$Br$_2$, which gave good quality ESR spectra. For L = 4-methyl-, 3,4-dimethyl-, and 3,5-dimethyl-pyridine, Cd(Mn)L$_4$-Br$_2$ was stable at room temperature, but gentle heating *in vacuo* gave Cd(Mn)L$_2$Br$_2$, with good ESR spectra. The 3-methylpyridine complex decomposed to a material of indefinite stoichiometry which gave a poor spectrum. All attempts to make Cd(Mn)(3-methylpyridine)$_2$Br$_2$ by other methods were unsuccessful.

Analyses (Imperial College Microanalytical Service) for C, H, N and halide were satisfactory for all compounds.

ESR Spectra

These were obtained as described previously [3].

Acknowledgements

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