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Ligand Dependence of the Polymeric Structure for $CdLCl_2$ (L = Substituted Pyridine)

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Abstract

Compounds of the type $CdLX_2$ (L = substituted pyridine, X = halide) have been studied by ESR spectra of the manganese-doped complexes, and shown to have the double-stranded polymeric structure found for $CdimidazoleCl_2$. There appear to be steric constraints on the formation of this structure, and no compounds of this type could be made with 3,5-disubstituted pyridines. Zero-field splitting parameters are reported for the complexes.

Introduction

We have recently shown [1] that the ESR spectra of manganese-doped compounds $CdLX_2$ (L = pyridine or methylpyridine, X = Cl or Br) are consistent with a double-stranded chain polymer structure, and suggested that this technique provides a criterion for recognition of such a structure. There was, however, a measurable difference between the zero-field splitting found for the complexes of pyridine itself, and those with methylpyridine. It seemed worthwhile to measure the spectra for the complexes formed with a range of substituted pyridines, to determine whether this structure persists, and to assess the variation of zero-field splitting with the bonding ability and steric requirements of the ligands.

Results

ESR spectra at both X- and Q-band frequencies have been obtained for the compounds $Cd(Mn)LX_2$ (L = pyridine, 3- and 4-methyl-, and 3,4-dimethylpyridine, X = Cl and Br; L = 3-cyano-, 3-hydroxy-, 3-chloro-, 3-bromo- and 3-ethyl, 4-methyl-pyridines, and isoquinoline, X = Cl).

The X-band spectra of the chlorides of stoichiometry $CdLCl_2$ were all rather similar, with a wealth of bands from below 100 to near 600 mT. This is similar to the observation for $CdpyCl_2$, and first order perturbation theory suggests that D = *ca.* 0.06 cm^{-1}, where D is the axial zero-field splitting parameter in the spin Hamiltonian (eqn. (1)):

$$\mathcal{H} = g\beta BS + D\left(S_z^2 - \frac{35}{12}\right) + E(S_x^2 - S_y^2) + SAI \qquad (1)$$

More precise values of D and of $\lambda(= E/D)$ for the individual compounds were found by comparison of the observed resonance field values at both X- and Q-band with those calculated using the program ESRS [2], by exact diagonalisation of the matrix derived from eqn. (1), with $g_{iso} = 2.00$. The results for two of the compounds, chosen to represent high and low values of the axial distortion, are given in Tables I–IV, in which the levels are labelled 1–6 in order of decreasing energy.

TABLE I. Q-band ESR Spectrum (mT) of $Cd(Mn)(3\text{-}Et,4Me\text{-}py)Cl_2$

Observed (ν = 34.002 GHz) B	Calculated for $D = -0.056$ cm^{-1}, $\lambda = 0.05$ B	Field direction	Levels	
979.5	974.8	z	6	5
1084.8	1079.8	y	2	1
1096.0	1094.7	z	5	4
Overlap of transitions	1116.3	x	2	1
	1142.8	y	3	2
	1159.9	x	3	2
1209.3	1208.1	x	4	3
	1209.3	y	4	3
Overlap of transitions	1214.6	z	4	3
	1261.1	x	5	4
	1279.8	y	5	4
	1319.5	x	6	5
1334.3	1334.5	z	3	2
1351.4	1354.8	y	6	5
1461.1	1454.5	z	2	1

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TABLE II. Q-band ESR Spectrum (mT) of Cd(Mn)(3-OHpy)-Cl_2

Observed (ν = 33.883 GHz) B	Calculated for $D = -0.0645$ cm^{-1}, $\lambda = 0.065$ B	Field direction	Levels	
932.8	934.2	z	6	5
1048.0	1049.4	y	2	1
1070.8	1072.2	z	5	4
	1104.2	x	2	1
1123.8	1124.3	y	3	2
1147.0	1149.8	x	3	2
Region	1201.5	x	4	3
of	1203.6	y	4	3
overlap	1210.2	z	4	3
1260.5	1259.8	x	5	4
1287.0	1288.0	y	5	4
	1325.5	x	6	5
1348.6	1348.4	z	3	2
1377.8	1378.3	y	6	5
1485.0	1486.7	z	2	1

TABLE III. X-band ESR Spectrum (mT) of Cd(Mn)(3-Et, 4-Mepy)Cl_2

Observed (ν = 9.475 GHz) B	Calculated for $D = 0.056$ cm^{-1}, $\lambda = 0.05$ B	Field direction	Levels	
68.7	69.3	$\theta = 72, \phi = 90$	4	1
	69.5	$\theta = 90, \phi = 80$	4	1
Region	98.9	z	6	5
of	121.4	$\theta = 21, \phi = 0$	5	2
overlap	129.8	$\theta = 29, \phi = 90$	5	2
180	190.6	$\theta = 56, \phi = 0$	5	3
	207.7	$\theta = 60, \phi = 90$	5	3
216.9	216.0	y	2	1
Region	218.6	z	5	4
of	248.1	$\theta = 16, \phi = 90$	4	2
overlap	252.4	x	2	1
262.7	264.8	y	3	2
272.7	278.6	x	3	2
314.5	316.5	x	4	3
318.0	321.6	y	4	3
	338.3	z	4	3
Region	369.6	x	5	4
of	390.3	y	5	4
overlap	447.9	x	6	5
460.1	458.2	z	3	2
490.0	481.8	y	6	5
576.0	578.4	z	2	1

TABLE IV. X-band ESR Spectrum (mT) of Cd(Mn)(3-OH-py)Cl_2

Observed (ν = 9.475 GHz) B	Calculated for $D = -0.0645$ cm^{-1}, $\lambda = 0.065$ B	Field direction	Levels	
	63.0	z	6	4
66.1	65.0	$\theta = 65, \phi = 90$	4	1
	65.8	$\theta = 90, \phi = 50$	4	1
Overlapping				
transitions	117.3	$\theta = 27, \phi = 0$	5	2
to: 140	131.0	$\theta = 36, \phi = 90$	5	2
192.5	191.3	$\theta = 54, \phi = 0$	5	3
	194.9	y	2	1
Region	200.8	z	5	4
of	217.9	$\theta = 60, \phi = 90$	5	3
overlap	248.8	x	2	1
to:	250.0	z	4	2
251.8	252.3	y	3	2
	255.8	$\theta = 11, \phi = 0$	4	2
267.9	264.4	$\theta = 15, \phi = 90$	4	2
	271.3	x	3	2
311.5	309.2	x	4	3
317.1	318.5	y	4	3
338.6	338.3	z	4	3
Region	365.9	x	5	4
of	397.6	y	5	4
overlap	459.3	x	6	5
481.1	476.1	z	3	2
510.0	509.8	y	6	5
611.0	614.9	z	2	1

The X-band spectra for these compounds show weak absorption near 125 mT, which are assigned as spin-forbidden bands, mainly the 5–2 transition in the *xz* and *yz* planes. These occur at resonance fields which vary little over a wide range of angles, and therefore appear much more strongly in the powder spectrum than might be expected from their low single-crystal transition probabilities. Indeed, their observed intensities are comparable with the weakest spin-allowed bands.

With these low *D*-values, the whole range of the spectrum was observed at X-band, and for most of the chlorides the hyperfine splitting was sufficiently well-resolved that the sign of *D* could be determined. In each case the average spacing of the hyperfine components was greater on the lowest-field allowed transition than on the highest field band. For example, for Cd(Mn)(3-bromopyridine)Cl_2 the mean spacing on the band at 94.7 mT was 9.4 mT, while that on the 582.5 mT band was 7.8 mT. This implies that *D* and *A* in eqn. (1) must have the same sign. The hyperfine spacing within a sextet invariably increased from low to high field for all the bands where it could be measured (in some cases overlapping of bands precluded such measurement). Thus, as normally found for manganese(II) the sign of *A* is negative, and *D* is also required to be negative.

Considerably more difficulty was found in preparing manganese-doped bromo-complexes of stoichiometry $CdLBr_2$. In most cases the reaction products gave ill-defined ESR spectra possibly indicative of mixtures. Only for pyridine itself and the methyl- and dimethyl-substituted pyridines were satisfactory spectra obtained. Those at X-band were very complicated, with considerable overlapping of transitions, and the better-resolved Q-band spectra (Fig. 1) were used to determine the values of D and λ. The results for 3,4-dimethylpyridine are shown in Table V. A negative sign for D has been assumed by analogy with the chlorides, since it was not possible to determine this sign for the bromides. The D-values obtained gave computer-simulated X-band spectra in good agreement with the observed spectra (Fig. 2).

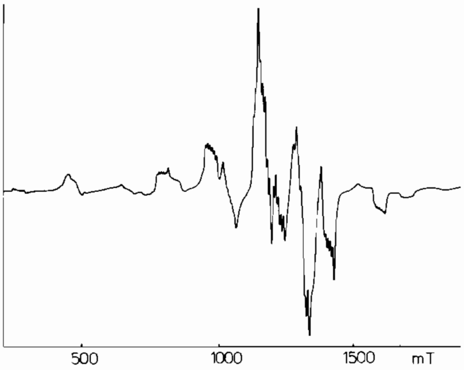

Fig. 1. Q-band (34 GHz) ESR spectrum of Cd(Mn)(3,4-dimethylpyridine)Br_2.

TABLE V. Q-band ESR Spectrum (mT) of Cd(Mn)(3,4-Me_2-py)Br_2

Observed (ν = 33.898 GHz) B	Calculated for $D = -0.180$ cm^{-1}, $\lambda = 0.07$ B	Field direction	Levels
249.7	252.3	$\theta = 90, \phi = 65$	4 1
	252.5	$\theta = 74, \phi = 90$	4 1
436.5	432.6	$\theta = 22, \phi = 0$	5 2
	441.5	z	6 5
470.5	467.7	$\theta = 25, \phi = 90$	5 2
657.0	661.0	$\theta = 56, \phi = 0$	5 3
742.5			
783.5	786.9	y	2 1
826.4	825.7	z	5 4
	951.7	x	2 1
962.3	963.7	y	3 2
1141.0	1143.5	x	3 2
Overlap	1163.3	y	4 3
1211.6	1210.1	z	4 3
1310.0	1306.1	x	4 3
1398.9	1397.7	y	5 4
1536.3	1539.4	x	6 5
1590.3	1595.3	z	3 2
1692.6	1693.0	y	6 5
	1982.2	z	2 1

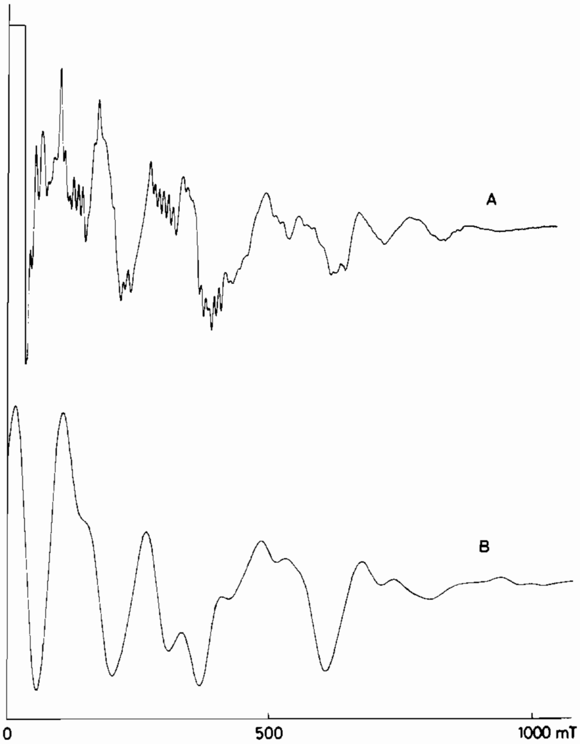

Fig. 2. (a) X-band (9.5 GHz) ESR spectrum of Cd(Mn)(3,4-dimethylpyridine)Br_2. (b) Computed spectrum for $D = 0.180$ cm^{-1}, $\lambda = 0.07$.

Discussion

No X-ray structural results are available for these compounds with pyridines as ligands, because they are not readily available as single crystals. However, an X-ray study [3] of CdimidazoleCl_2 has shown it to have the double-strand polymeric structure postulated [1, 4, 5] for these compounds. Cd(Mn)imidazoleCl_2 gives spectra at both X- and Q-band which are very similar to those of the pyridine complexes (Fig. 3) and which can be fitted with $D = 0.0645$ cm^{-1} and $\lambda = 0.045$. The slightly higher value of D compared with the pyridine ligands is to be expected in view of both the higher basicity of imidazole, and its smaller bulk. The general strong similarity to the pyridine compounds provides good evidence that the structure of all these compounds $CdLX_2$ is of the double-chain polymer type.

Values of D and λ for all the compounds are collected in Table VI. The D values show less variation with ligand than was found for the compounds Cd(Mn)L_2X_2, where the variations were related to both steric effects and the pK_a values of the ligands [6]. For the compounds described here, the base strength of the ligand appears to have little effect, the lowest D value being found for 3-ethyl, 4-methyl-

TABLE VI. Zero Field Splitting Parameters for the Complexes

L	D (cm^{-1})	λ
$Cd(Mn)LCl_2$		
Pyridine	0.0631	0.03
3-Mepyridine	0.0585	0.05
4-Mepyridine	0.0576	0.045
3,4-Dimepyridine	0.058	0.02
3-Cyanopyridine	0.058	0.015
3-Hydroxypyridine	0.0645	0.065
3-Chloropyridine	0.0576	0.06
3-Bromopyridine	0.057	0.065
3-Et,4-Mepyridine	0.056	0.05
Isoquinoline	0.0591	0.035
Imidazole	0.0645	0.045
$Cd(Mn)LBr_2$		
Pyridine	0.182	0.06
3-Mepyridine	0.185	0.08
4-Mepyridine	0.189	0.07
3,4-Dimepyridine	0.180	0.07

pyridine, which has a fairly high basicity, but considerable steric bulk.

When the chloro-complexes are prepared from ethanol or acetone solution, the initial product is normally CdL_2Cl_2, which on heating *in vacuo* loses 1 mol of ligand to give $CdLCl_2$. For all the 3,4-disubstituted ligands, however, $CdLCl_2$ precipitates immediately, and no compounds CdL_2Cl_2 were obtained. In contrast to this, the 3,5-disubstituted ligands readily gave compounds CdL_2Cl_2. but on heating *in vacuo* these decomposed to $CdCl_2$, with no $CdLCl_2$ being formed. Samples which analysed as $CdLCl_2$, formed by stopping the decomposition without the sample attaining a constant weight, gave spectra indicative of two Mn^{II} sites, one similar to that in CdL_2Cl_2, the other with high intensity at $g_{eff} = 2$, indicating a nearly regularly cubic structure (Fig. 4). This would be consistent with a mixture of CdL_2Cl_2 and $CdCl_2$.

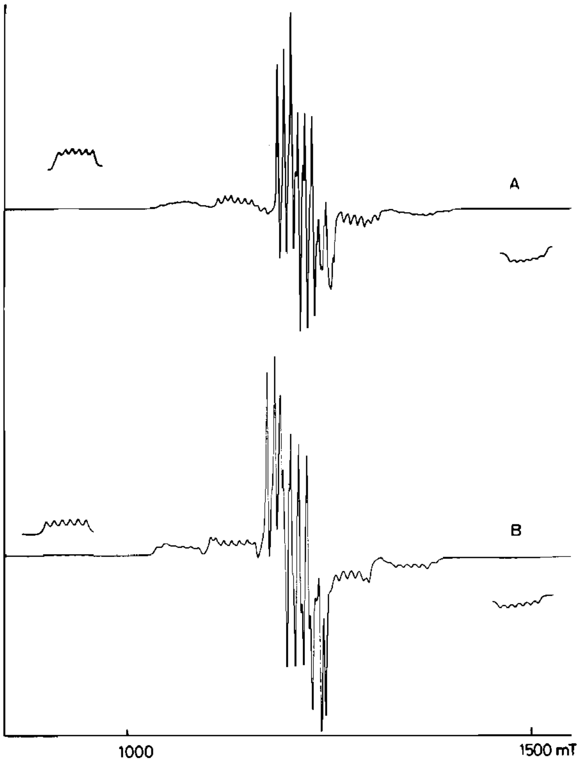

Fig. 3. Q-band ESR spectra of: (a) Cd(Mn)(3,4-dimethylpyridine)Cl_2; (b) Cd(Mn)(imidazole)Cl_2.

In chain polymers of the type postulated for these compounds, it seems likely that substituents, especially in the 3- and 5-positions, may interfere with ligands on adjacent metal ions. To relieve this, a bond-lengthening would be necessary, either of the M–N bond, or of the M–Cl bridging bonds. The stability of the Cd–Cl chain, which we find to be an important feature of cadmium chemistry, may

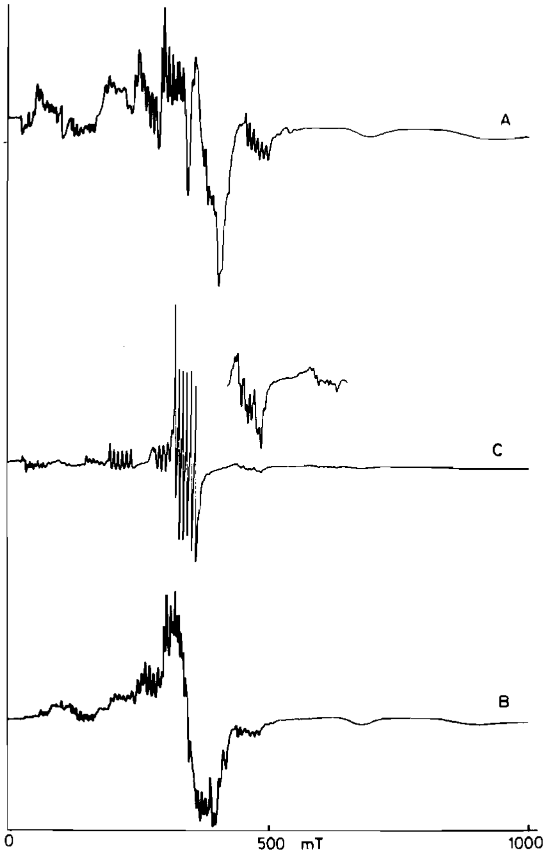

Fig. 4. X-band ESR spectra of (a) Cd(Mn)(imidazole)Cl_2; (b) Cd(Mn)(3-chloropyridine)Cl_2; (c) Product obtained by heating Cd(Mn)(3,5-dimethylpyridine)$_2Cl_2$ to give stoichiometry Cd(Mn)(3,5-dimethylpyridine)Cl_2.

favour the lengthening of the Cd–N bond. For 3-substitution this should lead to *D*-values lower than for pyridine, as generally found, and for 3,5-disubstitution the whole structure may be destabilised.

For the bromo-complexes a much smaller range of compounds was available. However it appears that steric constraints are rather less than for the chlorides, as *D*-values for mono-substituted pyridines were higher than for pyridine itself, in line with their higher pK_a values, and a reduced *D* was found only with disubstitution. It seems possible that the longer metal-metal distances for dibromo-compared with dichloro-bridges reduced the constraints on the neutral ligands. However, even in this case no complexes $CdLBr_2$ could be prepared with 3,5-disubstituted pyridines.

Experimental

Preparation of Cd(Mn)LCl_2

For all of the ligands used except the 3,4-disubstituted (including isoquinoline) these complexes were made by thermal decomposition of the corresponding 2:1 complex. The 2:1 complexes and the 1:1 complexes with 3,4-disubstituted ligands were made by adding to a stirred solution in ethanol of cadmium and manganese chlorides either the neat ligand (if liquid) or a solution of the ligand in ethanol. The precipitated products were filtered and washed with ethanol. Throughout, 2,2-dimethoxypropane was added to all solutions to remove any water. The manganese(II) ions are present at a nominal level of 1%.

Preparation of Cd(Mn)(3,4-dimethylpyridine)Br_2

This was made by thermal decomposition of the 4:1 complex. This high-stoichiometry complex was itself made by recrystallising cadmium and manganese bromides from 3,4-dimethylpyridine to which a little 2,2-dimethoxypropane had been added to remove water.

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

ESR Spectra

These were obtained as described previously [1].

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