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Electron Spin Resonance Study of Manganese(II) Ions in $M(N_2H_4)_2X_2$

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E.s.r. spectra are described of the hydrazine-bridged polymeric complexes $M(Mn)(N_2H_4)_2X_2$ *(M = Zn, Cd; X = Cl, Br or I) and of* $Hg(Mn)(N_2H_4)_2Br_2$*. The spectra are interpreted in terms of the zero-field splitting parameters D and* λ *(=* E/D*). D increases with ligand field distortion in the series Cl < Br < I, and is consistently greater for the zinc than for the cadmium complexes. The symmetry is close to axial in all cases. The mercury complex is shown to have the same polymeric structure as the zinc and cadmium compounds.*

Introduction

The e.s.r. spectra of manganese doped samples have proved to be useful probes of stereochemistry for the group IIB metals. This is particularly true where the metal–ligand and metal-anion stretching vibrations are difficult to study, on account, for example, of strong intra-ligand transitions in the low-energy region, such as those of hydrazine.

The complexes $M(N_2H_4)_2X_2$ (M = Mn, Zn or Cd; X = Cl, Br or I) are isomorphous, and comprise chains of hydrazine-bridged MX_2 units parallel to the *c*-axis of the crystal [1]. In contrast, the corresponding mercury complex $Hg(N_2H_4)_2Cl_2$ has been considered, on infrared spectral evidence, to contain a two-coordinate cation $Hg(N_2H_4)_2^{2+}$, with monodentate hydrazine [2]. We describe here an e.s.r. study of manganese(II) ions doped into the zinc and cadmium polymers, and also into $Hg(N_2H_4)_2Br_2$.

Experimental

Preparation of Compounds

$M(Mn)(N_2H_4)_2Cl_2$ (M = Zn, Cd)

A solution of the metal chlorides in hydrazine hydrate was added to stirred ethanol.

$Zn(Mn)(N_2H_4)_2Br_2$

This was obtained on dropwise addition of hydrazine hydrate to a boiling solution of $ZnBr_2$ and $MnBr_2 \cdot 4H_2O$ in methanol.

$Cd(Mn)(N_2H_4)_2Br_2$

A hot acetone suspension of $CdBr_2 \cdot 4H_2O$ and $MnBr_2 \cdot 4H_2O$ was added to excess hydrazine hydrate in acetone.

$Hg(Mn)(N_2H_4)_2Br_2$

An ethanol solution of $HgBr_2$ and $MnBr_2 \cdot 4H_2O$ was added to the stoichiometric quantity of hydrazine hydrate in the same solvent.

$Zn(Mn)(N_2H_4)_2I_2$

A solution of ZnI_2 and $MnI_2 \cdot 4H_2O$ in acetone containing a few drops of 2,2-dimethoxypropane was refluxed briefly, then an acetone solution of excess hydrazine hydrate was added dropwise.

$Cd(Mn)(N_2H_4)_2I_2$

An ethanol solution of CdI_2 and $MnI_2 \cdot 4H_2O$ containing a few drops of 2,2-dimethoxypropane was refluxed briefly and added to the stoichiometric amount of hydrazine hydrate in ethanol.

All the compounds precipitated immediately. Analyses (H and N, Microanalytical Laboratory, Imperial College) were satisfactory except for $Cd(Mn)(N_2H_4)_2Br_2$, for which the ratio of ligand to metal was always less than 2. The e.s.r. spectra of these samples indicated the presence of a substantial amount of an undiluted manganese species giving a broad signal at $g_{eff} = 2$. However, the anisotropic e.s.r. spectrum, which was fully reproducible over several different preparations, is considered to originate from the major constituent of the product, *viz.* $Cd(Mn)(N_2H_4)_2Br_2$.

E.s.r. spectra were obtained on polycrystalline samples at room temperature, as described previously [3].

Results

Spectra were obtained at both X- and Q-band for all six of the isomorphous complexes $M(Mn)(N_2H_4)_2X_2$ (where M = Zn or Cd; X = Cl, Br or I), and for $Hg(Mn)(N_2H_4)_2Br_2$. Nominal dopings of 1% and 5% manganese gave virtually identical spectra. There was,

TABLE I. Q-band E.s.r. Spectrum (mT) of $Zn(Mn)(N_2H_4)_2Cl_2$.

Observed (ν = 35.865 GHz)	Calculated for D = 0.29 cm^{-1}, λ = 0.015			
	B	T.P.[a]	Field Direction	Levels
236 m	234.3	0.5	$\theta = 60°, \phi = 90°$	6–3
~450m[b]	474.5	1.9	$\theta = 40°, \phi = 90°$	5–2
	481.6	1.1	$\theta = 60°, \phi = 90°$	5–3
659w	660.3	8.0	z	3–2
747 m	752.5	5.4	y	6–5
806 m	807.1	5.5	x	6–5
930 s	933.8	7.9	y	5–4
~950 m	950.8	7.9	x	5–4
1154 m	1156.1	8.4	x	4–3
1166 ms	1168.8	8.4	y	4–3
strong overlapping	1424.9	7.5	x	3–2
absorption	1459.2	7.6	y	3–2
1400–1600				
1937 w,br	1902.2	8.0	z	5–4
	1965.7	5.3	y	2–1

[a] T.P. = Single crystal transition probability. [b] Complex band with at least 2 sets overlapping hyperfine components.

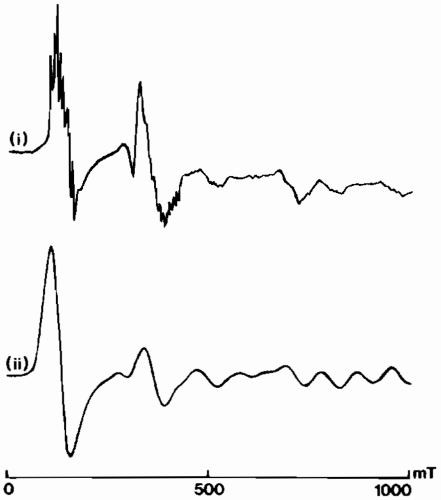

Fig. 1. E.s.r. spectrum (9.512 GHz) of $Zn(Mn)(N_2H_4)_2Cl_2$. (i) Experimental; (ii) calculated for D = 0.29 cm^{-1}, λ = 0.015.

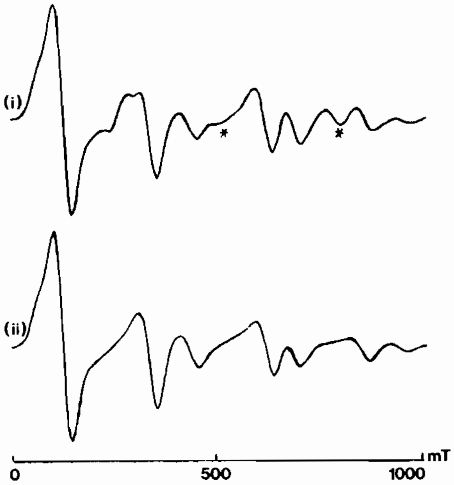

Fig. 2. Calculated X-band spectra for D = 0.24 cm^{-1}, λ = 0: (i) using 93 angles per octant in the icosahedral approximation; (ii) with magnetic field directions chosen at 1° intervals along one line of arc from pole to equator.

however, a tendency for the spectra to show an extra band, sometimes strong, near g_{eff} = 2, which is considered to be due to magnetically concentrated manganese(II) contaminants. In some cases it proved impossible to eliminate this. Except in the case of $Cd(Mn)(N_2H_4)_2Br_2$ (*vide supra*) these impurities were not detected in the analysis, and may well be undiluted $Mn(N_2H_4)_2X_2$, which all give only g_{eff} = 2 signals.

The anisotropic spectra were interpreted using the 'simplified' spin-Hamiltonian (1) in which

$$\mathcal{H} = g\beta B\cdot S + D(S_z^2 - 1/3\, S^2) + E(S_x^2 - S_y^2) \qquad (1)$$

g is assumed to be isotropic and equal to 2.00. Because of the complexity of the wave functions, the levels are labelled 1–6 in decreasing order of energy.

At X-band, the chlorides both give fairly complicated spectra, with bands extending to about 1000 mT (Fig. 1). It is noteworthy, however, that only three of these bands are due to 'along axis' transitions, and estimation of the zero field splitting parameters D and λ (= E/D) was achieved by curve simulation using the program [4] SHAPE 9. There was some difficulty in achieving a good fit, since all reasonable values of the parameters predicted extra

TABLE II. Assignment of Resonance Fields (mT) at ν = 9.521 GHz for D = 0.24 cm^{-1}, λ = 0.

Extremum in calculated spectrum of Fig. 2 (ii)	Calculated single crystal turning-point	T.P.	Field Direction	Levels
125.0[a]	126.0	5.2	x, y	6–5
366.2 (min)	355.4	5.4	x, y	4–3
469.1 (min)	458.5 (min)	5.4	θ = 14°	5–4
654.3 (min)	644.0 (max)	5.6	θ = 63°	3–2
720.1 (min)	706.3 (min)	4.2	θ = 28°	4–3
888.8 (min)	877.8	7.0	x, y	2–1
983.4 (min)	971.3 (max)	4.4	θ = 8°	5–4

[a] Field measured at point where trace crosses base-line.

TABLE III. Experimental and Calculated Resonance Fields (mT) for $Hg(Mn)(N_2H_4)_2Br_2$ at X-band.

Observed (ν = 9.525 GHz)	Calculated for D = 0.67 cm^{-1}, λ = 0.006			
	B	T.P.	Field Direction	Levels
116 vs	112.1	4.92	y	6–5
	117.8	5.34	x	6–5
350 vw	340.5	9.00	z	6–5
552 mw	553.0	4.40	x	4–3
593mw	593.4	4.40	y	4–3
ca. 900 vw	901.3	2.38	xz, yz planes θ = 10°	5–4
1278 w	1281	4.84	xz, yz planes θ = 55°	3–2

bands, not observed experimentally, near 530 and 800 mT (marked with * in Fig. 2). However, calculations for the axial case (λ = 0) using a different method of spherical averaging, show that these two bands are an artefact of the icosahedral approximation (Fig. 2). For the second calculation, the points on the sphere defining the directions in which B is to be applied were chosen at 1° intervals on one line of arc from pole to equator. This procedure gives a lineshape superior to that of the icosahedral method, but is of course limited to the axial case. Using this method the 'best fit' D values are found to be 0.29 cm^{-1} for the zinc and 0.24 cm^{-1} for the cadmium complex.

Apparent splitting of the band at about 130 mT (g_{eff} = 6) cannot, at these D values, be used to estimate the value of λ. The 5–4 transition in the yz plane lies below 100 mT for D < *ca.* 0.2 cm^{-1}, but moves upfield with increasing axial distortion, and is virtually coincident with the 6–5 (x, y) transition (g_{eff} = 6) when D = 0.24 cm^{-1}. The splitting of the band at 800–900 mT (2–1 in the xy plane), if this can be observed, is therefore, a more reliable guide to the degree of rhombic distortion. For both the chlorides λ appears to be about 0.015.

These parameters were then used to calculate the resonant fields at Q-band, by exact diagonalisation of the matrix derived from the spin Hamiltonian (1), using the program ESRS [3]. The values are compared in Table I with the experimental figures for $Zn(Mn)(N_2H_4)_2Cl_2$. It is noteworthy that the three lowest-field bands are due to spin forbidden transitions, which have appreciable intensity in these powder spectra. They are in fact stronger than the outermost spin-allowed transitions.

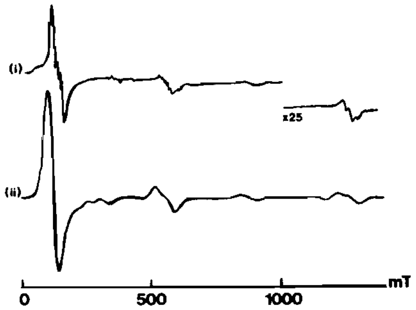

Fig. 3. E.s.r. spectrum (9.532 GHz) of $Hg(Mn)(N_2H_4)_2Br_2$. (i) Experimental; (ii) calculated for D = 0.67 cm^{-1}. λ = 0.006.

With this confirmation that the parameters were reasonably correct, an assignment was made of the bands in the calculated X-band spectrum. The results are shown in Table II. Only the bands at 125, 366

TABLE IV. Q-band E.s.r. Spectrum (mT) of $Zn(Mn)(N_2H_4)_2I_2$.

Observed (ν = 35.73 GHz)	Calculated for D = 1.21 cm^{-1}, λ = 0.019			
	B	T.P.	Field Direction	Levels
413 s,r[a]	415.7	4.9	y	6–5
489 s,r	491.2	6.1	x	6–5
~634 m,p	653.5	2.3	θ = 20°, ϕ = 90°	5–4
~670 w,p	669.6	0.67	θ ~ 10°, ϕ = 0	5–4
b	1404.9	4.9	x	4–3
1597 m,r	1599.2	5.0	y	4–3

[a] r = well resolved, 6-line hf structure; p = poorly defined hf structure. [b] g_{eff} = 2 region obscured by broad, strong absorption.

TABLE V. Q-band E.s.r. Spectrum (mT) of $Cd(Mn)(N_2H_4)_3I_2$.

Observed (ν = 35.725 GHz)	Calculated for D = 1.18 cm^{-1}, λ = 0.01			
	B	T.P.	Field Direction	Levels
430 m,r[a]	432.5	5.25	y	6–5
468 s,r	472.4	5.79	x	6–5
710 m,p	b			
g_{eff} = 2 region obscured by broad, v. strong absorption				
1437 m,r	1436.4	4.97	x	4–3
1532 m,r	1535.5	4.99	y	4–3

[a] See footnote a to Table IV. [b] Off-axis transition; see Table IV.

and 889 mT arise from transitions with the magnetic field along a tensor axis, and these are all 'perpendicular' transitions.

The X-band spectra of the bromides are much simpler (Fig. 3), those for the cadmium and the mercury compounds being indistinguishable. In addition to the strong g_{eff} = 6 band (6–5 transition in the xy plane) the 4–3 perpendicular band is prominent and well resolved, with hyperfine sextets centred on 552 and 593 mT. This permits immediate determination of D and λ as 0.67 cm^{-1} and 0.006 respectively. The splitting of the g_{eff} = 6 band due to the slight rhombicity of the field is too small to be detected experimentally (Table III).

In the zinc compound hyperfine structure is less well resolved, precluding accurate determination of band positions, and λ could not be determined, though it is clearly near to zero. The D value is a little higher than for cadmium and mercury, the best fit of the simulated spectrum being obtained with D = 0.71 cm^{-1}.

All samples prepared of the iodides contained an impurity giving a broad, unresolved band at g_{eff} = 2, probably the undiluted manganese complex $Mn(N_2H_4)_2I_2$ since it was undetected by analysis.

TABLE VI. Zero Field Splitting Parameters for Mn^{II} in $M(N_2H_4)_2X_2$.

M	X	D/cm^{-1}	λ
Zn	Cl	0.29	0.015
Cd	Cl	0.24	0.015
Zn	Br	0.71	*ca.* 0
Cd	Br	0.67	0.006
Hg	Br	0.67	0.006
Zn	I	1.21	0.019
Cd	I	1.18	0.010

In the Q-band spectra, assignment of the weak but well-resolved sextets at 1400–1600 mT to x, y (4–3) leads to the parameters of Tables IV and V. The lack of well-resolved hyperfine structure on the bands at 600–700 mT is in accord with their assignment as off-axis transitions.

In the X-band spectra the g_{eff} = 6 transition is clearly more split for the zinc than for the cadmium complex, in agreement with the higher λ value. The higher field bands, however, were broad, and their positions were difficult to measure with any precision, so no real confirmation of the D values was possible, though the approximate band positions corresponded reasonably well with the calculated positions (observed for the zinc complex *ca.* 650 and 900 mT, calculated 668 and 933 mT; observed for the cadmium complex *ca.* 720 and 840 mT, calculated 720 and 856 mT). It should also be pointed out that the assumptions of $g_{iso} = 2.00$ and the cubic field term *a* vanishingly small may not be justified for iodide complexes, but too few bands were observed to justify an attempt to vary these parameters to achieve a better fit to the experimental spectra.

Discussion

The axial distortion clearly increases in the order Cl < Br < I, as expected, and as found previously [5] for manganese in Mpyridine_4X_2. The parameters obtained (Table VI) are comparable with, but a little higher than, those found for the pyridine systems, in line with the slightly higher ligand field strength of hydrazine. The λ values are all close to zero, although the site-symmetry of the manganese ion is necessarily lower than axial. It seems that an assumption of axial symmetry is justified in interpreting the spectral properties of these compounds.

The D-values are consistently higher for the zinc than for the analogous cadmium compounds. This effect has been noted with other ligands, and is almost certainly due to the size of the lattice site available to the manganese ion. The difference, though, appears to decrease somewhat from chlorides to iodides.

Most striking is the similarity in spectra between $Cd(Mn)(N_2H_4)_2Br_2$ and $Hg(Mn)(N_2H_4)_2Br_2$. It seems very unlikely that this could arise by chance, and the resolution of the spectrum shows that it is not due to undiluted $Mn(N_2H_4)_2Br_2$. The evidence points strongly to a polymeric 6-coordinate structure for the mercury compound. Since its infrared spectrum is very similar to that reported by Brodersen [2] for $Hg(N_2H_4)_2Cl_2$, with ν(N–N) at 952 cm^{-1}, it seems that the evidence for the monomeric structure of the latter compound should be re-examined.

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