Electron Spin Resonance Spectra of Manganese(II) Ions in Trigonal Complexes of Protonated 1,4-Diazabicyclo[2.2.2]octane

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E.s.r. spectra are reported for manganese(II) ions doped into the polycrystalline complexes $[Ni(HL^+)_2Cl_3]Cl$, $[Ni(HL^+)_2Br_3]Br$, and $[Zn(HL^+)Cl_3]$ (L = 1,4-diazabicyclo[2.2.2]octane) and the zero-field splitting parameters D and λ are calculated. All the three complexes give spectra interpretable in terms of an essentially trigonal field, but the two chloro-complexes show significant deviations from truly axial symmetry. All the three spectra show bands of appreciable intensity due to ' off-axis ' transitions.

THERE is continuing interest in five-co-ordinate complexes of bivalent first-row transition-metal ions. These complexes are generally obtained by the use of multidentate ligands specifically tailored to induce five-co-ordination, complexes involving exclusively unidentate ligands being far less common. An interesting family of complexes of the latter type has the general formula [1] $[M^{II}(R\text{-}L^+)_2X_3]Y$ (M = Mn, Fe, Ni, or Cu; L = 1,4-diazabicyclo[2.2.2]octane; X = Cl or Br). Electronic spectroscopy and magnetic measurements on the powdered solids indicate the presence in each case of a MN_2X_3 chromophore of basically trigonal-bipyramidal geometry.[1]

A recent X-ray diffraction study of $[M^{II}(N\text{-Me-}L^+)_2Cl_3][ClO_4]$ (M = Ni or Cu), intended to precede more detailed spectroscopic work, shows, however, that the cations are so arranged in the pseudo-cubic unit cell as to rule out the feasibility of anisotropy measurements on orientated single crystals.[2] We are prompted, therefore, to report the powder e.s.r. spectrum (at X-band frequency) of manganese(II) ions doped into the closely related complex $[Ni(HL^+)_2Cl_3]Cl$, which gives an electronic spectrum identical with that of $[Ni(N\text{-Me-}L^+)_2Cl_3][ClO_4]$. Spectra have also been obtained of Mn^{II} in $[Ni(HL^+)_2Br_3]Br$, and in pseudo-tetrahedral $[Zn(HL^+)Cl_3]$, the cobalt and nickel isomorphs of which gave electronic spectra interpretable on a C_{3v} model.[3] Each of the three host complexes is X-ray isomorphous with its manganese(II) analogue. The e.s.r. results indicate, for the two chloro-complexes, a small but definite departure from trigonal symmetry which is not detectable by the spectroscopic techniques employed in the earlier studies.

RESULTS AND DISCUSSION

(*i*) $[(Zn,Mn)(HL^+)Cl_3]$.—A large number of transitions is observed, with absorption spreading from 0 to *ca.* 800 mT, the majority of the transitions showing clearly defined manganese nuclear hyperfine (h.f.) splitting (Figure 1). The highly irregular h.f. pattern on the lowest band (0—70 mT) is noteworthy, as is the very poor h.f. resolution at 500—640 mT. For the remaining bands the resonant fields agree well with values calculated, using the program [4] ESRS, by exact diagonalisation of the matrix derived from the spin Hamiltonian (1), for $D = 0.19$ cm^{-1}, $\lambda = E/D = 0.04$, $g_{iso.} = 2.00$, and for magnetic-field directions parallel to the principal

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

D-tensor axes (Table). In each case the experimental resonance fields were measured at the midpoint of the first and last of the six approximately evenly spaced hyperfine lines.

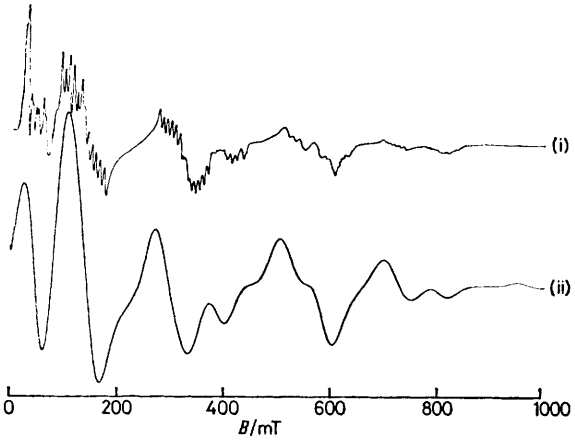

FIGURE 1 E.s.r. spectra (9.175 GHz, 0—1 000 mT) of $[(Zn,Mn)(HL^+)Cl_3]$: (*i*) experimental, (*ii*) calculated for D = 0.19 cm^{-1}, λ = 0.04, and linewidth = 40 mT

X-Band spectrum (mT) of $[(Zn,Mn)(HL^+)Cl_3]$

Obs. (ν = 9.175 GHz)	Calc. for D = 0.19 cm^{-1}, λ = 0.04			
	B	T.P.[a]	Field direction	Levels [b]
0—70s [c]	38.8	2.8	θ 40°, ϕ 90°	5—4
	43.5	1.1	θ 20°, ϕ 0°	5—4
107.5s	106.9	5.0	y	6—5
152.0s	154.8	6.46	x	6—5
291.0m	292.4	5.74	x	4—3
347.0m	347.8	5.80	y	4—3
404.0m [d]				
Broad, medium intensity	577.1	4.6	θ 30°, ϕ 0°	4—3
absorption 500.0—640.0	613.1	4.8	θ 30°, ϕ 90°	4—3
711.5w	713.8	6.27	x	2—1
794.0w	801.1	6.03	y	2—1

[a] T.P. = Transition probability calculated as in ref. 6. [b] The levels are numbered 1—6 in order of decreasing energy. [c] Resolved but irregular h.f. structure. [d] Poorly defined h.f. structure.

The bands showing anomalous or unresolved hyperfine structure are then seen to correspond to single-crystal turning points other than those along the principal axes. The association of irregular or poorly defined h.f. structure with ' off-axis ' transitions appears to be fairly common, and can be a valuable aid in band assignment.[5] The effect may be ascribed to the appreciable intensity, at intermediate orientations of the magnetic field, of nuclear-forbidden ($\Delta m_I \neq 0$) h.f. lines which in powder spectra may not be resolved from the ' allowed ' lines.

The calculated lineshape (see below) of Figure 1 gives satisfactory agreement with experiment, and serves to confirm the correctness of the assigned spin-Hamiltonian parameters.

(*ii*) $[(\mathrm{Ni,Mn})(\mathrm{HL}^+)_2\mathrm{X}_3]\mathrm{X}$ (X = Cl *or* Br).—Both these complexes give spectra with the most intense band near $g_{\mathrm{eff.}} = 6$. The spectral linewidths observed are higher than for $[(\mathrm{Zn,Mn})(\mathrm{HL}^+)\mathrm{Cl}_3]$. Hyperfine splitting is weakly resolved on the main band in the case of $[(\mathrm{Ni,Mn})(\mathrm{HL}^+)_2\mathrm{Cl}_3]\mathrm{Cl}$ (Figure 2), but is otherwise absent. Spectra of this type have heretofore been interpreted using D–B plots[6] (for $B \parallel x,y,z$), but the inadequacies of this method are now recognised and may be summarised as follows. (*a*) Off-axis single-crystal turning points may contribute substantially to powder absorption, as has been demonstrated above for $[(\mathrm{Zn,Mn})(\mathrm{HL}^+)\mathrm{Cl}_3]$. (It may be noted here that Aasa has replotted the diagrams to include some of the off-axis lines.[7]) (*b*) D–B plots do not accurately indicate the relative intensities of the bands in the spherically averaged spectrum; only the transition probability at the single-crystal turning point is known and this has been shown to be less important, generally, than the orientation of the magnetic field and the rate of bending at the turning point. (*c*) As is shown by Figure 2, accurate location of resonance-field positions from first-derivative experimental spectra becomes very difficult when the separation between adjacent singularities in the powder pattern is comparable with the linewidth.

It is clear, therefore, that simulation of at least part of the experimental spectrum, as is commonly attempted for $S = \frac{1}{2}$ systems, is essential for accurate determination of the spin-Hamiltonian parameters.[8]

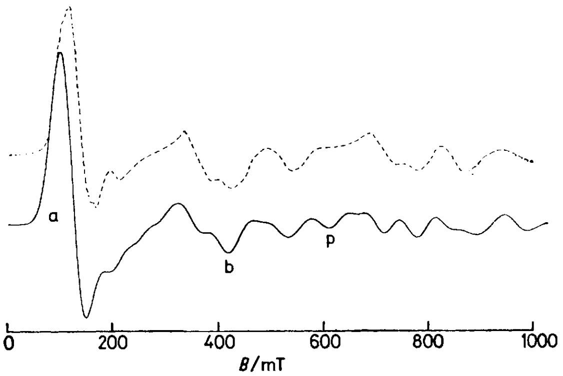

FIGURE 2 E.s.r. spectra (9.50 GHz, 0—1 000 mT) of $[(\mathrm{Ni,Mn})(\mathrm{HL}^+)_2\mathrm{Cl}_3]\mathrm{Cl}$: (— — —) experimental; (——) calculated for $D = 0.31\ \mathrm{cm}^{-1}$, $\lambda = 0.03$, and linewidth = 40 mT

The spectrum of $[\mathrm{Ni}(\mathrm{HL}^+)_2\mathrm{Cl}_3]\mathrm{Cl}$ (Figure 2) shows a qualitative resemblance to that of $[\mathrm{Cu^I(PPh_3)_2}]_3[\mathrm{Fe^{III}(S_2C_2O_2)_3}]$ for which D has been estimated[9] at $0.24\ \mathrm{cm}^{-1}$; in the present complex, however, the splitting of bands b and d is evidence for a non-axial D tensor.

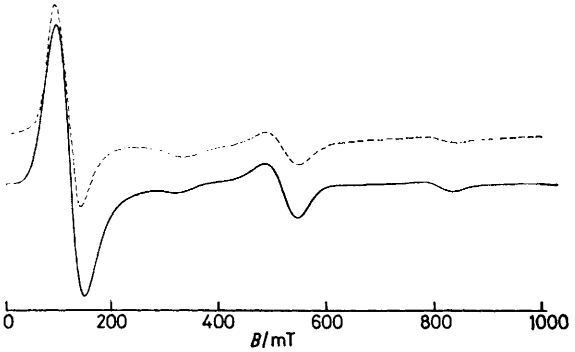

FIGURE 3 E.s.r. spectra (9.18 GHz, 0—1 000 mT) of $[(\mathrm{Ni,Mn})(\mathrm{HL}^+)_2\mathrm{Br}_3]\mathrm{Br}$: (— — —) experimental; (——) calculated for $D = 0.60\ \mathrm{cm}^{-1}$, $\lambda = 0$, and linewidth = 50 mT

The lineshape calculated for $D = 0.31\ \mathrm{cm}^{-1}$ and $\lambda = 0.03$ generally agrees well with the experimental spectrum and at least one of the discrepancies, *viz.* the enhanced intensity of band p in the lower spectrum, is demonstrably an artefact of the method of simulation. It is worth pointing out that bands a and b are the only ' along-axis ' transitions of the spectrum.

The spectrum of the bromide complex (Figure 3) shows, in addition to the $g_{\mathrm{eff.}} = 6$ transition characteristic of an axial or near-axial species, prominent absorption around 500 mT which is ascribed to x,y 4—3. Neither of these bands is discernibly split, and any rhombicity of the D tensor must be very small ($\lambda < 0.01$). The weak high-field band (*ca.* 800 mT) arises from an off-axis transition. The observed spectrum is well fitted by the parameters $D = 0.60\ \mathrm{cm}^{-1}$ and $\lambda = 0$.

EXPERIMENTAL

The complexes were prepared by literature methods,[1,3] but using *ca.* 1 mol % manganese(II) in the reaction mixture. All had good analyses. Since the complexes were somewhat hygroscopic, spectra were obtained for several different, freshly prepared, samples of each complex, and checked for reproducibility. The spectrometer has been described previously.[4]

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