Manganese(II) Ions as Stereochemical Probes in Reactions of Zinc Halides with Pyrazine

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Pyrazine is shown to form complexes $[Zn(pyz)_2X_2]$ (pyz = pyrazine, X = Cl or Br) as well as the previously known $[Zn(pyz)X_2]$. E.s.r. spectra of these compounds doped with manganese(II) ions show the stereochemistry to be polymeric with pyrazine bridges, and the doping technique permits identification of the complexes even in mixtures.

Despite several reports of the complexes $[M(pyz)_2Cl_2]$ (pyz = pyrazine), where M is a first series transition metal, no record exists of the preparation of analogous complexes of zinc, cadmium, or mercury. It has been claimed, in fact, that so long as adequate pyrazine is present in the reaction mixture, complexes $[M(pyz)X_2]$ (X = halogen) are obtained, irrespective of the metal : pyrazine ratio.[1] The only reported [1] complex of a different stoicheiometry is $[Zn(pyz)_{\frac{3}{2}}Br_2]$, believed to be the decomposition product of an unstable complex, $[Zn(pyz)_2Br_2]$.

Where unusual stoicheiometries are encountered, it is frequently difficult to establish whether the compounds are pure, or contain a mixture of species. We show here that for diamagnetic compounds of divalent ions, doping of the lattice with manganese(II) and observation of the e.s.r. signals can be of great help in identifying the species present. The existence of stable compounds $[Zn(pyz)_2X_2]$ (X = Cl or Br) is shown in this way, and analysis of the spectra permits deduction of the stereochemistry around the metal ion.

Results and Discussion

Reaction of zinc chloride or bromide with pyrazine in 1 : 2 molar ratio in acetone or alcohols yielded solids of variable composition, corresponding to formulae $[Zn(pyz)_nX_2]$, with $1 < n < 2$. With reduction in the quantity of pyrazine, the composition of the product approached that of the known complexes with $n = 1$, although pure products were reproducibly obtained only with ligand : metal ratios as low as 1 : 5. With the use of increasing amounts of pyrazine, however, the composition gradually approached limiting values of n of $\frac{7}{4}$ for the chloride, and 2 for the bromide. These were attained with the use of at least 4—5 mol of pyrazine per mol of metal ion.

These compounds were prepared in the presence of 1 mol % of manganese halide, and the e.s.r. spectra of the products were studied. All the samples gave well resolved spectra with hyperfine structure on at least some of the bands. This shows that the manganese ions have entered the host lattice, rather than forming a separate phase, which would give either broad, ill defined lines, or, if polymeric, a single band at $g_{eff.} = 2$.

At X-band frequency, $[Zn(Mn)(pyz)_2Br_2]$ gives a simple spectrum, with only four bands in the range 0—1 400 mT, of which two, at 115 and 605 mT, show well defined hyperfine structure. This is typical of axial or near-axial species, with D in the range *ca.* 0.6—0.75 cm^{-1}; D is the zero-field splitting parameter in the spin-Hamiltonian (1) in which g is assumed isotropic and equal to 2.00. Because of the considerable mixing of wavefunctions, it is inappropriate to designate the energy levels by the value of M_s. Instead, they are labelled 1—6 in decreasing order of energy.

Table 1. Q-Band e.s.r. spectrum of $[Zn(Mn)(pyz)_2Br_2]$

	Calculated for $D = 0.75\ cm^{-1}, \lambda = 0.0$			
Observed [a] B/mT	B/mT	T.P.[b]	Field direction	Levels
ca. 148 (s) [c]	154.0	2.0	$\theta = 28°$	5–4
314 (w)	320.4	8.0	z	6–4
493 (s)	501.0	5.4	xy	6–5
1 253 (s)	1 259.2	5.8	xy	4–3
1 285 (m)	1 286.0	9.0	z	6–4
1 593 (w) [c]	1 590.9	5.8	$\theta = 15°$	5–4

[a] ν = 36.000 GHz. Intensities are in parentheses. [b] Transition probability. [c] Irregular hyperfine structure.

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

For $[Zn(Mn)(pyz)_2Br_2]$, no splitting was observable in the bands at 115 and 605 mT, which may be assigned as the 6–5 and 4–3 transitions respectively, both in the xy plane. The value of λ (equal to E/D) is, therefore, very close to zero, and the band positions suggest $D = ca.\ 0.75\ cm^{-1}$. The Q-band spectrum, which shows more bands, is well fitted by these parameters (Table 1, Figure 1).

With zinc chloride the limiting stoicheiometry obtained using a large excess of pyrazine was $[Zn(pyz)_{\frac{7}{4}}Cl_2]$, which could of course indicate a mixture of $[Zn(pyz)Cl_2]$ and $[Zn(pyz)_2Cl_2]$ in 1 : 3 molar ratio. However, the e.s.r. spectra of the manganese-doped samples showed no signal due to $[Zn(Mn)(pyz)Cl_2]$, though this was present in the samples of unreproducible composition obtained when less pyrazine was used in the preparation (Figure 2).

The compound reproducibly obtained gives a complicated X-band e.s.r. spectrum with its strongest band at *ca.* 125 mT, and weaker bands extending to about 1 000 mT (Figure 2). Such a spectrum is characteristic of axial or near-axial species with D in the range *ca.* 0.2—0.5 cm^{-1}. The richer and better resolved Q-band spectrum permitted determination of the zero-field parameters as $D = 0.24\ cm^{-1}$, $\lambda = 0.005$ (Table 2). Simulation of the X-band spectrum for these parameters using the program [2] SHAPE9 showed good agreement with the experimental spectrum (Figure 2), although only three of the observed transitions were ' along-axis,' and these were all in the xy plane (Table 3).

Figure 1. Q-Band spectrum of [Zn(Mn)(pyz)$_2$Br$_2$]: (*a*) experimental spectrum; (*b*) calculated for $D = 0.75$ cm^{-1}, $\lambda = 0$

Table 2. Q-Band e.s.r. spectral data for [Zn(Mn)(pyz)$_2$Cl$_2$]

	Calculated for $D = 0.24$ cm^{-1}, $\lambda = 0.005$			
Observed[a] B/mT	B/mT	T.P.[b]	Field direction	Levels
254 (m)	250.7	5.0	z	3–1
467 (m)	471.0	1.0	$\theta = 30°$, $\varphi = 0$	5–2
479 (m)	475.0	1.0	$\theta = 30°$, $\varphi = 90°$	5–2
483 (m)				
769 (w)	765.7	7.9	z	3–2
834 (m)	836.6	5.3	y	6–5
851 (m)	852.0	5.3	x	6–5
990 (ms)	992.4	7.8	y	5–4
	997.9	7.8	x	5–4
1 187 (s)	1 188.2	8.5	x	4–3
	1 190.8	8.5	y	4–3
1 279 (w)	1 279.7	8.9	z	4–3
	1 438.0	7.7	x	3–2
1 450 (vs)	1 447.1	7.7	y	3–2
1 796 (w,br)	1 793.8	7.9	z	5–4
	1 815.4	5.2	x	2–1
1 833 (w)	1 829.9	5.2	y	2–1

[a] $\nu = 35.825$ GHz. Intensities are in parentheses. [b] Transition probability.

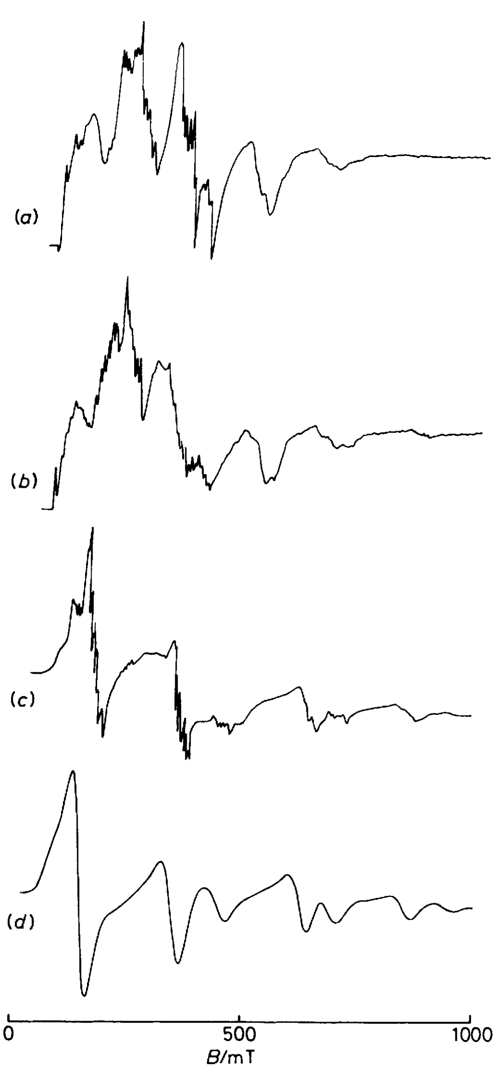

Figure 2. X-Band e.s.r. spectra of (*a*) [Zn(Mn)(pyz)Cl$_2$]·0.5H$_2$O; (*b*) product of a preparation using a ZnCl$_2$: pyz ratio of 1 : 2; (*c*) [Zn(Mn)(pyz)$_2$Cl$_2$]; (*d*) calculated for $D = 0.24$ cm^{-1}; $\lambda = 0$

Table 3. X-Band e.s.r. spectral data for [Zn(Mn)(pyz)$_2$Cl$_2$]

	Calculated for $D = 0.24$ cm^{-1}, $\lambda = 0$		
Observed * B/mT	B/mT	Field direction	Levels
ca. 85	85.5	$\theta = 20°$	5–4
ca. 120	126	xy	6–5
360	355	xy	4–3
480	459	$\theta = 14°$	5–4
650	644	$\theta = 63°$	3–2
695	706	$\theta = 28°$	4–3
860	878	xy	2–1

* $\nu = 9.521$ GHz.

These parameters are very similar to those found[3] for [M(Mn)(N$_2$H$_4$)$_2$Cl$_2$] (M = Zn or Cd) in which the metal ion is surrounded by a N$_4$Cl$_2$ octahedron. The bromo-complex is also similar to the corresponding hydrazine complexes. We therefore suggest that [Zn(pyz)$_2$Br$_2$] has a pyrazine-bridged octahedral structure, and that the main component of [Zn(pyz)$_{\frac{7}{4}}$Cl$_2$] is [Zn(pyz)$_2$Cl$_2$] with a similar structure. The contaminant is probably either ZnCl$_2$·xH$_2$O, which has limited solubility in acetone, or some form of hydrous zinc oxide or oxo-chloride.

It is clear that the [Zn(pyz)$_2$X$_2$] compounds are neither halide-bridged polymers, which give very much lower D values than those observed here, not tetrahedral complexes which give X-band spectra with the main intensity at $g_{\text{eff.}}$ *ca.* 4. For example, [Cd(Mn)(py)$_2$X$_2$] (X = Cl or Br, py = pyridine) which have halide bridges, give D values of 0.125 and 0.30 cm^{-1} respectively,[4] while tetrahedral complexes such as [Mn(qn)$_2$Br$_2$] (qn = quinoline) have λ values [5] near to 0.3. The difference in the X-band spectra is very obvious, and can be detected without calculation of precise parameters.

Contrary to earlier reports, the compound [Zn(pyz)$_2$Br$_2$] is stable in air at room temperature, and no species [Zn(pyz)$_{\frac{3}{2}}$Br$_2$] has been detected in this study.

Experimental

Preparation of [Zn(Mn)(pyz)$_2$Br$_2$].—A suspension of anhydrous zinc bromide, plus *ca.* 1 mol % MnBr$_2$·4H$_2$O, in acetone, was added slowly to a stirred solution of pyrazine in the same solvent, the metal : ligand ratio being 1 : 5. The precipitated solid was filtered off and air-dried (Found: C, 25.2; H, 2.0; N, 14.9. $C_8H_8Br_2N_4Zn$ requires C, 24.9; H, 2.1; N, 14.5%).

The compound approximating to [Zn(Mn)(pyz)$_2$Cl$_2$] was prepared similarly from propan-1-ol (Found: C, 30.0; H, 2.5; N, 18.4. $C_8H_8Cl_2N_4Zn$ requires C, 32.4; H, 2.7; N, 18.9%).

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

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