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Vibrational Spectra of Zinc Pyrazine Complexes

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The infrared spectra of pyrazine (pyz) complexes of transition metals have been the subject of much interest, and several studies of $MpyzX_2$ and $Mpyz_2X_2$ (X = Cl or Br) have been reported, but Raman results are lacking. For zinc and cadmium, only the $MpyzX_2$ type has been studied in the infrared [1–3], and the only Raman data reported were for $CdpyzCl_2$ [3].

We report here an infrared and Raman study down to 50 cm-’ on $Znpyz_2X_2$ and $ZnpyzX_2$ (X = Cl and Br), a discussion of their stereochemistry, and some assignment of the lower energy bands.

Results

In all the complexes the apparent lack of coincidences of infrared and Raman bands in the region (400-1600 cm-‘) of the pyrazine fundamentals suggests that the centre of symmetry of the ligand molecule is retained, which implies that it acts as a bridging ligand between two metal ions. Pyrazine has no fundamentals below 400 cm^{-1}.

Znpyrazine₂ X₂

The marked similarities between the spectra of the two compounds suggests that they are isostructural. A strong halide-sensitive band which appears in the infrared spectra at 238 cm-’ (chloride) and 160 cm^{-1} (bromide) lies within the range expected for $\nu(Zn-X_{terminal})$ in octahedral ZnL_4X_2, and is quite inconsistent with the presence of tetrahedral $Znpyrazine_2X_2$, or octahedral complexes with halide bridges. These compounds appear therefore to be structurally similar to $Copyrazine_2Cl_2$, which has a polymeric sheet structure with bridging pyrazine molecules [4].

Five infrared active modes are predicted for this structure, of which two are essentially stretching (one M-N and one M-X) and three are deformation modes. The five bands observed for each complex are therefore readily assigned as in Table I. Those assigned as ν(Zn–N) and δ(N–Zn–N) are virtually unchanged on change of halide, while δ(N–Zn–X) moves to lower frequency in the bromide, although, predictably, the shift is less marked than for ν(Zn–X). All the bands appear at lower frequency than in the cobalt complexes [5].

TABLE I. Low Energy Vibrational Spectra of $Znpyrazine_2X_2$.

IR	ν(M–X)	ν(M–N)	δ(N–M–N)	δ(N–M–X)
$Znpyz_2Cl_2$	238s	196m	145s, 126m	114m
$Znpyz_2Br_2$	160m	196m	142sh, 128m	103m
Raman	ν(M–X)	ν(M–N)	δ(N–M–X)	Other Bands
$Znpyz_2Cl_2$	219s	195s	128s	71s, 51sh
$Znpyz_2Br_2$	131s	195s	112s	228m[a], 77s

[a] See text for discussion of this band.

Raman spectra for complexes $Mpyz_2X_2$ have not previously been reported, and results for our complexes are given in Table I. Of the five bands seen for each compound, one, at 195 cm^{-1}, is independent of halide, and almost coincident with the infrared-active ν(Zn–N). In the factor group D_{4h} used to assign the IR spectra of $Copyz_2X_2$, no such coincidence should occur, and there should be only one Raman-active ν(M–X). Clearly there are more bands to be explained in the zinc complex. Tilting of the pyrazine rings would lower the symmetry within a sheet, and it seems most reasonable to assign the band at 195 cm^{-1} as ν(Zn–N). This leads to assignment of ν(Zn–Cl) at 219 cm^{-1} and ν(Zn–Br) at 131 cm-‘.

Comparisons are not readily available, since most complexes of nitrogen heterocycles with zinc halides adopt tetrahedral structures. However, these values seem reasonable compared with the infrared bands at 238 and 160 cm^{-1} respectively. The bands at 128 and 112 cm^{-1} for chloride and bromide respectively are then assigned as deformation modes, probably involving motion of the halide, while the bands below 100 cm^{-1} may well involve lattice modes, and we make no attempt to assign them. The medium-intensity band at 228 cm-’ for the bromide is not assigned at present but is discussed below.

ZnPyrazineX₂

The infrared spectrum of $ZnpyzCl_2$ has previously been reported by Child *et al.* [1] and by Ferraro *et al.* [2]. Both quote bands at about 216 and 162 cm^{-1}; the latter also give a shoulder at 194 and a weak band at 102 cm-‘. Our work confirms the presence of the low-energy band, which is below the range studied by Child *et al.*, but we do not see the shoulder at 194 cm^{-1}. We observe in addition a shoulder at 255 cm-’, which we assign as a component of ν(M–Cl), by analogy with the complexes $MpyzCl_2$ (M = Mn, Fe, Co and Ni) all of which have a band or shoulder in the range 245-261 cm-’ [1].

The Raman spectrum has not previously been reported. It shows two strong bands at 218 and 181 cm-’ in the metal-ligand stretching region. The

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structure of this compound is considered [2, 6] to be similar to that of $CdpyzCl_2$, which has pyrazine molecules bridging $[CdCl_2]_n$ chains, giving sheets of symmetry D_{2h} [3]. The vibrational modes for this type of structure have been listed [3]. On this basis the Raman bands may be assigned as Zn-Cl stretches, with that at higher energy most probably the a_g mode, since it lies close in energy to the corresponding band for cadmium, and probably involves little, if any, motion of the metal ion. Our complete assignments for the metal ligand stretches of $ZnpyzCl_2$ are therefore as in Table II.

The corresponding bromide is considered [1, 2] to have a polymeric tetrahedral structure, with bridging pyrazines. Our infrared spectrum agrees with those previously reported [1, 2] and the Raman spectrum (Table III) shows approximate coincidences, as expected.

On the basis of an approximate C_{2v} symmetry at the metal ion, nine vibrational bands due to skeletal modes are expected, and nine are seen above 90 cm^{-1}. In the metal-ligand stretching region, we assign the two strongest Raman bands to the a_1 modes. These are fairly close in energy, and might be expected to be coupled. However, the work of Child *et al.* [1] on the IR spectrum has shown that the band at 230 cm^{-1} is deuteration-sensitive, whereas that at 206 cm-’ is not. We therefore assign the lower band as essentially ν(Zn–Br). Assignment of the highest energy band (278 cm^{-1} in Raman and 270 cm-’ in IR) as the b_1 ν(Zn–Br) on the basis of its intensity, is also in agreement with the deuteration studies.

The lower energy bands involving deformation modes are difficult to assign with certainty. However, the band at 92 cm^{-1} is very close in energy to the Raman-active ν_4 deformation of the tetrahedral $ZnBr_4{}^{2-}$ ion. Since δ(Br–Zn–Br) might be expected at lower energy than the other deformation modes of the complex, we assign the 92 cm^{-1} band in this way.

The strongest Raman band for this compound is at 226 cm-‘. We suggest that the unexplained band at 228 cm-’ in the Raman spectrum of $Znpyz_2Br_2$, which is the weakest band in that spectrum, may be due to decomposition in the laser beam to give some $ZnpyzBr_2$.

TABLE II. Low Energy Vibrational Spectra of $ZnpyzCl_2$.

	ν(M–N)	ν(M–Cl)			Other Bands
	b_{2u}	a_g	b_{2g}	$b_{1u} + b_{3u}$	
IR	216s			255sh,162s	106m
Raman		218s	181s		

TABLE III. Low Energy Vibrational Spectra of $ZnpyzBr_2$.

Raman	IR	Tentative Assignment
49s		
61s		
68sh		
	84s	
92s		δ (Br-Zn-Br)
108s		
122s		
130sh		
184w		
217s	210m	a_1 ν(Zn–Br)
226vs	235sh	a_1 ν(Zn–N)
	257m	b_2 ν(Zn–N)
278w	270ms	b_1 ν(Zn–Br)

Experimental

Complexes were prepared as described previously [6, 7]. IR spectra (4000-200 cm-‘) were obtained on Perkin-Elmer 457 and 325 grating spectrometers using nujol or hexachlorobutadiene mulls between CsI plates. Low energy IR spectra (300-40 cm^{-1}) were obtained on a Beckman R.I.I.C. FS-720 interferometer using Vaseline mulls and polythene plates. Raman spectra of the powdered solids were obtained on a Cary model 81 spectrophotometer with a CRL 52 MG argon-krypton laser.

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