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The Far-infrared Spectra (450-80 cm⁻¹) of Octahedral Halogen-bridged Transition Metal(II) Complexes

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The far-infrared spectra of some complexes of the type MX_2L_2 and $MX_2(LL)$ [M = Mn, Fe, Co, Ni; X = Cl, Br, I; L = pyridine, quinoline, ammonia; LL = pyrazine] have been recorded at both liquid nitrogen temperature and room temperature, and assignments made of $\nu(M-X)$ and $\nu(M-N)$ modes. Two strong $\nu(M-X)$ bands are found as predicted for the infinite planar $[MX_2]_n$ chains present in these compounds. Contrary to previous reports, the $\nu(M-X)$ bands, even for the chloro-complexes occur below 220 cm⁻¹ for this type of system.

Introduction

The structural characterization of complexes of inorganic halides by low frequency infrared spectroscopy is now widespread.[1,2] However, in order to draw reliable conclusions from this technique, it is necessary to make reference to the spectra of compounds of known structure. Octahedral polymeric halogen-bridged complexes of transition metal(II) halides are common, but the only far-infrared studies of compounds known to have this structure were made over restricted ranges [above 200 cm⁻¹ (Refs. 3, 4), and 150 cm⁻¹ (chlorides only studied)[5]]. Since only tentative assignments were made in these previous reports, and as $\nu(M-Br)$ and $\nu(M-I)$ modes were below the instrumental limit[3,4] or unassigned,[5] we have studied in more detail (down to 80 cm⁻¹) the spectra of a number of complexes of metal(II) halides with pyridine (py), pyrazine (pyz), methylpyrazine (mpyz), quinoline (quin), and ammonia, which are of this structural type. The few previous assignments of $\nu(M-X)$ and $\nu(M-N)$ are shown to be unacceptable,* and new ones are proposed as given in Table I.

Experimental Section

The pyridine and pyridine-d_5 complexes, and NiCl₂-

quin₂ were prepared from solutions in absolute ethanol. The bisammines were prepared by thermal decomposition of the hexammines. The pyrazine complexes were obtained by thermal decomposition[6] of the bispyrazine compounds[7] using either a thermobalance (Stanton HT–SM, ca. 0.5 g sample) or bench-scale methods, with the exception of MnCl₂pyz which was prepared by mixing ethanolic solutions of MnCl₂, 4H₂O and pyrazine. Purity was established by elemental analysis. Analytical data for the monopyrazine complexes which have been reported but not well-characterized (MCl₂pyz; M = Mn, Co, Ni)[6] or which are new, are given in Table II. Complexes prepared by thermal decomposition showed no far-infrared bands due to starting materials.

The far-infrared spectra were recorded using a R.I.I.C. FS–520 interferometer, with the samples as pressed discs in polythene; the data were computed on an Elliott 4100 computer to a resolution of 5 cm⁻¹.

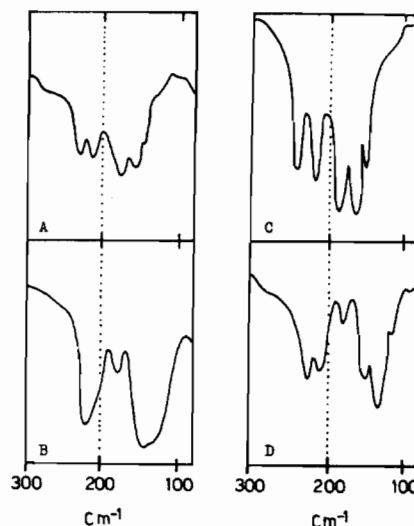Figure 1. Far-infrared spectra of: A, MnCl₂py₂ (RT). B, MnBr₂py₂ (RT). C, MnCl₂py₂ (LN). D, MnBr₂py₂ (LN). The dotted line at 200 cm⁻¹ shows the lower frequency limit of previous investigations.[3]

(*) Since the completion of this work, a report has appeared of the effect of high pressures on the far-infrared spectra of some octahedral complexes of cobalt(II) chloride and bromide (C. Postmus, J.R. Ferraro, A. Quattrochi, K. Shobatake, and K. Nakamoto, *Inorg. Chem.*, 8, 1851 (1969)). The assignments made on this basis are in agreement with those reported herein.

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(2) D.M. Adams, «Metal-Ligand and Related Vibrations», Arnold London (1967).
(3) R.J.H. Clark and C.S. Williams, *Inorg. Chem.*, 4, 350 (1965).
(4) R.J.H. Clark and C.S. Williams, *J. Chem. Soc. A*, 1425 (1966).
(5) C.W. Frank and L.B. Rogers, *Inorg. Chem.*, 5, 615 (1966).
(6) C. Beech and C.T. Mortimer, *J. Chem. Soc. A.*, 1115 (1967).
(7) A.B.P. Lever, J. Lewis, and R.S. Nyholm, *J. Chem. Soc.*, 1235 (1962); 5042 (1963); 4761 (1964).

Table I. Far-infrared Spectra of the Complexes (cm⁻¹)

Compound	Temp.ᵃ	ν(M—X)ᵇ		ν(M—N)			Other bands
MnCl₂py₂	RT	175 s	160 s	230 m	214 m		144 sh
	LN	183 s	163 s	238 s	217 s		145 m
MnBr₂py₂	RT	135 sbr		212 s		175 m	
	LN	147 m	135 s	225 m	210 m	180 w	115 w
MnCl₂pyz	RT	195 s	150 s	255 m	223 m		100 w
	LN	200 s	151 s	257 m	230 m		
MnBr₂pyz	RT	150 s	115 s	224 s	207 m		
	LN	154 s	122 s	235 s	210 m		114 w
FeCl₂py₂	RT	182 s	162 s	240 sh	227 m	220 sh	
	LN	202 m, 191 sh	172 sh, 162 s	244 m	229 s		
α—CoCl₂py₂	RT	188 s	167 s	245 sh	235 m	227 m	140 w
	LN	192 s	177 s	249 m	239 m	228 m	147 w
CoCl₂mpyz ᶜ	RT	206 s	172 s	252 s			145 w
	LN	211 s	172 s	260 s			
CoCl₂pyz	RT	201 s	177 s	247 s			
	LN	209 s	179 s	260 s			
CoBr₂pyz	RT	156 s	137 s	243 m	213 m		
	LN	165 s	140 s	253 s	220 s		
CoI₂pyz	RT	137 s	120 s	227 m	196 w		
	LN	141 s	129 s, 122 s	239 s			90 s
NiCl₂quin₂	RT	222 s	195 m	262 m			150 w
	LN	230 s	199 m	265 m			150 m, 110 w
NiCl₂py₂	RT	193 s	182 s	262 m	247 sh	237 m	154 w
	LN	197 s	185 s	267 m	248 m	240 m	220 sh, 154 w
NiBr₂py₂	RT	147 sbr		255 m	240 m	200 m	
	LN	155 s	141 m	258 m	245 s	205 m	
NiCl₂pyz	RT	214 s	192 s	260 m			178 w
	LN	220 s	195 s	270 s			182 w
NiBr₂pyz	RT	180 s	150 s	252 m	230 m		
	LN	182 s	150 s	264 m	235 m		
NiI₂pyz	RT	162 s	132 s	234 w	204 w		
	LN	167 s	140 s, 131 sh	244 m	214 m		
NiCl₂(NH₃)₂	RT ᵈ						150 m
	LN	187 sbr		210 sbr ᵉ			152 s
NiBr₂(NH₃)₂	RT	158 sh, 150 sh	135 s	187 s ᵉ			137 sh
	LN	160 s	140 s	190 s ᵉ			
NiI₂(NH₃)₂	RT	125 s	117 s	180 s ᵉ			140 sh
	LN	135 s	120 s	181·s ᵉ			

ᵃ RT = Room temperature, LN = —196°. ᵇ In-plane deformations of [MX₂]ₙ chains. ᶜ mpyz = methylpyrazine. ᵈ ν(MX) and δ(NMN) unresolved strong band 250-180 cm⁻¹. ᵉ δ(NMN) mode.

Table II. Analytical Data and Diffuse Reflectance Electronic Spectra for MX₂pyz Complexes

Compound	Colour	Weight loss (%)ᵃ Found	Required	Analyses (%) Found C	H	N	Required C	H	N	νmax (cm⁻¹)
MnCl₂pyz ᵇ,ᶜ	white	—	—	23.3	1.9	13.6	23.3	1.9	13.6	26300 w, 18200 w, 16100 w
MnBr₂pyz ᵈ	cream	—	—	16.3	1.5	10.1	16.3	1.4	9.5	7690 vw, 6170 vw
CoCl₂pyz ᵇ	violet	26.6	27.6	23.3	1.9	13.6	23.3	1.9	13.6	18500 m, 16950 m
CoBr₂pyz	grey	20.0	21.1	16.3	1.3	9.3	16.1	1.4	9.4	18200 m, 15900 m
CoI₂pyz	brown	16.8	16.5	12.2	1.0	7.0	12.2	1.0	7.1	16950 sh, 14900 m
NiCl₂pyz ᵇ	yellow-green	26.2	27.3	22.9	1.8	13.4	23.2	1.9	13.5	27000 sh, 14300 s, 8770 s, 7410 w
NiBr₂pyz	yellow	20.0	21.2	15.9	1.2	9.4	16.1	1.3	9.4	14300 s, 8700 s, 7410 w
NiI₂pyz ᵉ	brown	—	—	12.7	1.1	7.2	12.2	1.0	7.2	8130 m, 6900 m

ᵃ From thermal decomposition of bispyrazine complexes using thermobalance. ᵇ Previously reportedᵉ but not well-characterized. ᶜ Found: Cl, 34.2. C₄H₄Cl₂MnN₂ requires: Cl, 34.4%. ᵈ Found: Br, 54.3. C₄H₄Br₂MnN₂ requires: Br, 54.2%. ᵉ Found: I, 63.5. C₄H₄I₂N₂Ni requires: I, 64.6%.

Considerable improvement in the spectra took place on cooling the samples to liquid nitrogen temperature (*e.g.* Figure 1), with resolution of overlapping bands. However some frequency shifts took place, generally of those bands assigned (see Discussion) to modes involving motion of the bridging ligands (*i.e.* halogen and pyrazine), and for this reason frequencies at both ambient and liquid nitrogen temperature are included in Table I. Some new but weak features also appeared in some spectra as a result of band sharpening on cooling the samples. We have made the reasonable assumption that no structural changes take place on cooling; this is supported by the absence of gross changes in the spectra.

The diffuse reflectance electronic spectra were recorded on a Unicam SP700A spectrometer.

Results and Discussion

The crystal structure of α—CoCl₂py₂ has been shown to consist of symmetrical planar [MX₂]ₙ chains with

octahedral co-ordination completed by pyridine molecules.[8] The complexes MCl_2py_2 (M = Mn, Fe, Ni) and $MnBr_2py_2$ are isomorphous with α–$CoCl_2py_2$.[9] With the exception of the monopyrazine compounds, the other complexes listed in Table I have been previously shown[4,7,9,10] by means of electronic spectral and/or magnetic susceptibility measurements to have structures analogous to that of α–$CoCl_2py_2$.

The complexes MX_2pyz have electronic spectra (Table II) which are clearly typical of the octahedrally co-ordinated metal atoms.[7] For CoX_2pyz (X = Cl, Br, I), we have found that no coincidences occur of infrared and Raman bands due to « internal » modes of the pyrazine ligand, indicating the presence of a centre of symmetry and therefore that these complexes contain bidentate rather than monodentate pyrazine.[11] The structures of the pyrazine complexes are thus almost certainly analogous to those of the other complexes studied, with $[MX]_n$ chains linked by bidentate pyrazine molecules.[7]

Although many other members of the series of compounds listed in Table I are known, these are not generally of the same structural type. For example, the co-ordination of the metal atoms is tetrahedral in $CoBr_2py_2$, CoI_2py_2, NiI_2py_2, $CoBr_2mpyz$, CoI_2mpyz, and $NiBr_2quin_2$, whereas planar geometry is found for NiI_2quin_2.
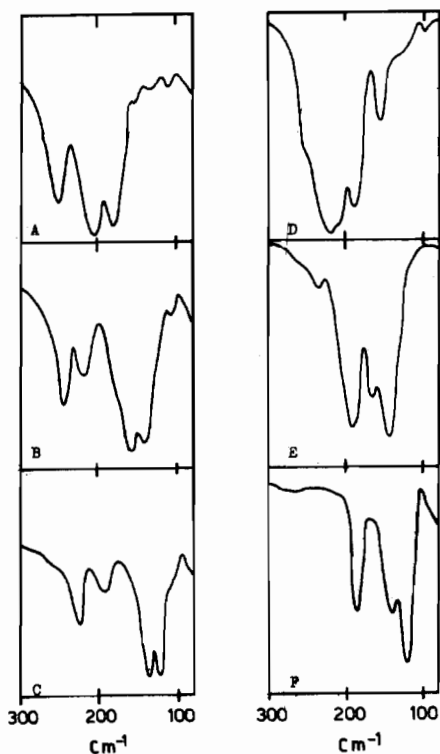

Figure 2. Far-infrared spectra of: A, $CoCl_2pyz$. B, $CoBr_2pyz$. C, CoI_2pyz. D, $NiCl_2(NH_3)_2$. E, $NiBr_2(NH_3)_2$. F, $NiI_2(NH_3)_2$. Spectra A, B, C recorded at ambient temperature; for D, E, F samples cooled to $-196°$.

The assignments given in Table I have been made by comparing chlorides, bromides, and iodides of corresponding complexes. Although mixing of vibrations of the same symmetry may occur, previous studies[1-5] have shown that the assignment of ' $\nu(M-X)$ ' and ' $\nu(M-L)$ ' in MX_nL_m complexes is reasonable. Thus $\nu(M-X)$ may be identified by their shift to lower frequencies when X is progressively changed from Cl→Br→I (see Figures 1, 2, and Table I). In halogen-bridged systems such as studied here, the ' $\nu(M-X)$ ' modes are best described as in-plane deformations of the M_2X_2 rings, as shown below. The former description has been used previously for other bridged species,[12-15] and is that used in the ensuing discussion for clarity. Those bands which are relatively insensitive to changes in X are attributed to $\nu(M-N)$ [except for the ammines, discussed below], since the organic ligands do not have fundamental modes in the regions where these bands are found. The slight X-dependence of the ' $\nu(M-N)$ ' modes arises from some coupling with vibrations of the $[MX_2]_n$ chains of the same symmetry class, but the assignment of these bands is supported by deuteration studies (see below).

For those chloro-complexes which do not have bromo- and iodo-analogues (e.g. α–$CoCl_2py_2$, $NiCl_2quin_2$), assignments may still be made with confidence because of the very close similarity of the spectra with those of the other metal dichlorides and of corresponding complexes with different amine ligands. Similarly, although ammonia is rather different from the other ligands studied, the $\nu(M-X)$ bands in the ammines are found at similar frequencies and form the same pattern as found for the other complexes. The spectra of the complexes $NiX_2(NH_3)_2$ show an additional band at 180-210 cm^{-1} which we attribute to a $\delta(N-M-N)$ mode by analogy with other ammines,[2] further, a deformation mode generally occurs at just under half the stretching frequency, which for these compounds is ca. 430 cm^{-1} (Ref. 4).
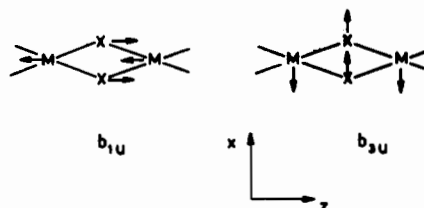

Figure 3. Infrared-active $\nu(M-X)$ modes of $[MX_2L_2]_n$ chains (both in plane). The L groups lie on the y-axis and are not shown.

A common way of dealing with the vibrations of chain polymers is to treat the problem in terms of the appropriate line group symmetry.[16,17] The $[MX_2L_2]_n$ chains present in the compounds now studied have a line group isomorphous with the point

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(15) D.M. Adams and P.J. Chandler, J. Chem. Soc. A, 588 (1969).

group D_{2h}, taking L as a point mass.[12,16,17] On this basis, eleven skeletal modes are predicted (cartesian axes as in Figure 3):

$$\Gamma^{line}(D_{2h}) = 2a_g(R) + b_{1g}(R) + b_{2g}(R) + b_{3g}(R) + 2b_{1u}(i.r.) + 2b_{2u}(i.r.) + 2b_{3u}(i.r.)$$

Using internal co-ordinates, we predict:

$$\Gamma^{line}_{MN}(D_{2h}) = a_g(R) + b_{2u}(i.r)$$

and

$$\Gamma^{line}_{MX}(D_{2h}) = a_g(R) + b_{2g}(R) + b_{1u}(i.r.) + b_{3u}(i.r.)$$

As pointed out above, these latter modes are really in-plane M_2X_2 deformations, as may be seen from Figure 3, where the approximate forms of the infra-red-active modes (b_{1u} and b_{3u}) are shown (see also Ref. 17). The other infrared-active modes predicted are an out-of-plane $[MX_2]_n$ chain (b_{2u}) and N—M—X angle deformations (b_{1u} and b_{3u}).

The line group treatment has been found to be satisfactory for other species which consist of $[MX_2]_n$ chains;[12,17] two $v(M—X)$ modes have been found in the infrared spectra of $CuCl_2$,[12,13] $CuBr_2$,[12,13] and $PdCl_2$,[13] in agreement with prediction.[12] Also, two bridging $v(M—X)$ infrared bands are found for the planar species $[M_2X_6]^{n-}$ (M = Pd, Pt; n = 2. M = Au; n = 0)[14] and $M_2X_4L_2$ (M = Pd, Pt).[15]

This treatment is a simplification, but the main features of the spectra should be predicted. Thus two strong $v[M—X]$ bands are generally found, although in a few cases some weaker features are also observed (Table I). However, in many cases the numbers of $v(M—N)$ bands identified were more than expected. In order to confirm these assignments, we have recorded the spectra of some pyridine-d_5 complexes. With $MBr_2(C_5D_5N)_2$ [M=Mn, Ni], all the bands of the corresponding pyridine-h_5 complexes which were assigned to $v(M—N)$ on the basis of their insensitivity to X (relative to the $v(M—X)$ modes) were found shifted to longer wavelengths. This supports the assignments given in Table I and is of particular significance in these cases since for these compounds the spread of $v(M—N)$ is greatest. The magnitudes of the shifts (Table III) show that the lowest frequency $v(M—N)$ band observed in each case should be assigned to the infrared forbidden (on the D_{2h} line group approximation) $v_s(N—M—N)$ mode (a_g), and the other $v(M—N)$ bands to v_{as}-(N—M—N) (b_{2u}). For the complexes $MCl_2(C_5D_5N)_2$ [M = Mn, Co, Ni], the spectra were not sufficiently well defined for the true individual band positions to be located accurately, but the overall absorption envelopes attributed to $v(M—N)$ were shifted to lower frequencies (1-5 cm^{-1}) compared with the corresponding pyridine-h_5 compounds.

For $\alpha—CoCl_2py_2$ (the only compound studied for which full crystallographic data are available), the pyridine rings are inclined to the $[CoCl_2]_n$ chain axis (by ca. 10°).[8] If this orientation is taken into account in the line group treatment, then the isomor-

phous point group is C_2. All the modes are thus allowed in both the infrared and Raman spectra. This then explains the activation of the $v_s(N—C—N)$ mode in the infrared, and will also account for the weak X-sensitive features observed.

However, in order to explain the appearance of the third $v(M—N)$ band, it is necessary to consider the packing of the polymer units in the crystal. The line group approximation is subject to the same limitations as the point group treatment for monomeric species in the solid state, and as an initial refinement the site symmetry approach of Halford[18] may be used. However, the C_2 symmetry of the chains of $\alpha—CoCl_2py_2$ (including pyridine orientations) is retained in the crystal,[8] so that the extra features observed in the spectra must have their origin in correlation splitting.

The crystallographic space group of $\alpha—CoCl_2py_2$ is $P2/b$ (C_{2h}^4), with four formula units, each from a different chain, in the primitive unit cell.[8] A factor group analysis[19] (Table IV) gives for the internal modes of the $[CoCl_2N_2]_n$ skeletons:

$$\Gamma^{cryst}(C_{2h}^4) = 10a_g + 12b_g + 10a_u + 12b_u$$

Eight of these may be described as $v(M—N)$ modes:

$$\Gamma^{cryst}_{MN}(C_{2h}^4) = 2a_g(R) + 2b_g(R) + 2a_u(i.r.) + 2b_u(i.r.)$$

The correlation between line and factor groups for these modes is as follows:

$$4a_g(D_{2h}) \longrightarrow 4a(C_2) \longrightarrow 2a_g + 2a_u(C_{2h}^4)$$

and

$$4b_{2u}(D_{2h}) \longrightarrow 4b(C_2) \longrightarrow 2b_g + 2b_u(C_{2h}^4)$$

Hence four $v(M—N)$ modes may appear in the infra-red spectrum of the crystal, two (a_u) originating from the $v_s(N—M—N)$ mode of the isolated polymer, and two (b_u) from the $v_{as}(N—M—N)$ mode. The deuteration studies described above show that this correlation splitting is observed only for the $v_{as}(N—M—N)$ mode.

The effect of correlation splitting on the $v(M—X)$ modes is, predictably, less than on $v(M—N)$. Indeed, as pointed out above, the appearance of more than two $v(M—X)$ modes in the infrared spectrum is consistent with C_2 line group symmetry. At the same time it is significant that three $v(M—X)$ bands are observed for two of the three iodides studied, since in these cases correlation splitting of $[MX_2]_n$ modes is likely to be greatest.

Conclusion

A line group treatment affords a satisfactory basis for interpreting the appearance of two strong $v(M—X)$ bands (in-plane deformations of $[MX_2]_n$ chains) in the infrared spectra of systems containing octahedral $[MX_2N_2]_n$ chains. Factor group splitting accounts for the number of $v(M—N)$ bands observed.

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(17) P. J. Lock, Ph. D. Thesis (University of Leicester, U.K.) (1968).

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(19) S.S. Mitra, Solid State Physics, 13, 1 (1962).

Table III. Metal-nitrogen modes of bis(pyridine-d_5) complexes of $MnBr_2$ and $NiBr_2$

Complex	Temp.	$\nu(M-N)$ (cm^{-1})	ν_H/ν_D (obs)	ν_H/ν_D (calcd.) [a] asym	sym
$MnBr_2(C_5D_5N)_2$	RT	210	1.01_0		
		170	1.02_9		
	LN	222	1.01_4	1.00_7	1.03_1
		207	1.01_4		
		173	1.04_0		
$NiBr_2(C_5D_5N)_2$	RT	237 [b]	1.01_3		
		191	1.04_7	1.00_8	1.03_1
	LN	242 [b]	1.01_2		
		198	1.03_5		

[a] Obtained by treating py—M—py unit as a linear triatomic system using equations given previously [G. Herzberg, « Infrared and Raman Spectra of Polyatomic Molecules », Van Nostrand, New York, p. 230 (1945)]. [b] The true band position of the higher frequency component of this absorption could not be placed accurately.

Table IV. Factor group analysis [a] of α—$CoCl_2py_2$, taking pyridine groups as point masses

Activity	C_{2h}^4	n	T	T'	R'	n_i [b]
Raman	a_g	14	0	2	2	10
Raman	b_g	16	0	4	4	12
Infrared	a_u	14	1	1	2	10
Infrared	b_u	16	2	2	4	12

[a] Symbols: n = total number of modes; T = number of acoustical translations; T' = number of optical translations; R' = number of external rotations; n_i = number of internal vibrations of $[CoCl_2N_2]_n$ chains. [b] Obtained by subtracting the number of acoustical and optical lattice modes from the total number of modes belonging to each irreducible representation. Note, however, that since n_i refers to a polymeric species, the only true rotational lattice modes are those involving rotation about the C_2 axes of the chains (*i.e.* those which are symmetrical to these axes, $2a_g + 2a_u$). Relative rotations of $CoCl_2N_2$ formula units about the other orthogonal axes will be internal modes ($4b_g + 4b_u$) of the chains (cf. line group treatment).

The spectra may be considered to be characteristic of octahedral $[MX_2N_2]_n$ chains. Even for chloro-complexes, these $\nu(M-X)$ bands generally occur below 200 cm^{-1}.

The few previous assignments[3-5] of $\nu(M-X)$ for this type of system with transition metals are not acceptable now that the spectral region has been extended and the resolution of the spectra increased by cooling the samples. For example, at room-temperature $MnCl_2py_2$ and $MnBr_2py_2$ give bands at 214 m, and 230 m, and 212 s, respectively. The band at 230 cm^{-1} was previously assigned to $\nu(M-Cl)$ since no band

was found in a corresponding position in the bromide.[3] However, at liquid nitrogen temperature the band in the bromo- complex at 212 cm^{-1} splits into two components of medium intensity at 210 and 225 cm^{-1} (Figure 1). Also, the general point must be made that all the bands in the spectral region studied show some degree of halogen-dependence which, if only a restricted spectral range (*e.g.* to 200 cm^{-1}) is available, makes assignment of ' $\nu(M-X)$ ' and ' $\nu(M-N)$ ' modes difficult.

Clearly, the correlations presented herein will be of most use when knowledge of the geometry of the metal environment is not sufficient to establish a structure e.g. 6-co-ordinate $MX_2(LL)_2$ complexes where LL is a potentially bidentate ligand. Recently, a number of studies on this type of complex have been reported, but in most cases far-infrared spectra were recorded to 200 cm^{-1} only.[20] From the present work it is clear that in order to obtain reliable evidence for halogen- (rather than LL-) bridging in these systems, it is necessary that the spectral region studied be extended to well below this limit.

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