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Far-Infrared and Raman Spectral Assignments for 1:1 Complexes of Metal Dihalides with Unidentate Ligands.
Double-Strand Halogen-Bridged Chain Structures of MX_2(pyridine) Polymers

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Far-infrared (30–350 cm^{-1}) and low frequency Raman spectra have been studied for a series of complexes MX_2(pyridine) where M = Mn, Co, Ni or Cd, and X = Cl or Br. Assignments of ν(MX) and ν(MN) modes have been made, assisted by noting shifts in the bands on replacing the pyridine ligand by pentadeuteriopyridine. The results are compatible with, and lend support to, a structure comprising double-strand halogen-bridged polymeric chains in which each metal atom is surrounded by one pyridine ligand, two bico-ordinate halogen atoms, and three trico-ordinate halogen atoms. The results provide the most definitive basis so far for structural diagnosis of compounds of this stoicheiometry.

Introduction

The literature contains reports of a large number of complexes of transition metal(II) salts with unidentate ligands, in which the metal:ligand ratio is 1:1, *i.e.* MX_2(L) adducts. Because of difficulties in obtaining samples suitable for single-crystal X-ray diffraction, definitive structural data on these systems are not common. Instead, inferences are usually drawn from measurements of magnetic susceptibility and electronic spectra concerning the co-ordination geometry, and far-infrared spectra are used to identify the metal–ligand vibrational modes and hence the geometrical arrangement of the metal–ligand bonds.

There are two aspects of this previous work which are not wholly satisfactory. In the first place, the types of organic ligands (L) which have been used cover a wide range and are often of such complexity that interpretation of the far-infrared spectra is hazardous and ambiguous. Additionally, even their mode of co-ordination is not always certain. The second main point which needs to be made is that nearly all the previous far-infrared studies were restricted to the spectral range above 200 cm^{-1}, whereas pertinent information, often the most diagnostic, is to be found in the 100–200 cm^{-1} region. In consequence, since previous work [1–3] has shown that erroneous assignments resulted from studies restricted to a 200 cm^{-1} limit in the case of $MX_2(pyridine)_2$ and $MX_2(pyridine)_4$ complexes, there remains the distinct possibility that a similar situation obtains for the 1:1 series. Certainly, the spectra of MX_2(L) complexes have not been subject to proper study hitherto.

We have therefore undertaken a detailed investigation of the series of complexes which may be regarded as the 'model system' for the 1:1 series, *viz.* MX_2(pyridine). Fragmentary reports of these compounds are scattered through the literature [4–14], but the structural data are not at all definitive and are certainly insufficient to use in structural diagnosis beyond specification of the metal co-ordination number. For only a few members of the series have far-infrared bands been reported [9, 10, 12], and there are no Raman data available. The compounds can only be made by thermal decomposition of 1:2 or 1:4 analogues, and because they are unstable to further thermal treatment and are insoluble in non-destructive solvents, samples suitable for single-crystal X-ray diffraction cannot be obtained. Low-frequency vibrational spectroscopy is thus the most amenable technique for determining their skeletal structures.

Results

The compounds studied in the present work are listed in Table I; all were obtained by heating the corresponding bis(pyridine) or bis(pentadeuteriopyridine)

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TABLE I. Preparative and Analytical Data.

Complex[a]	Colour	Weight loss (%)[b]		Calculated (%)			Found			Ref.
		Calc.	Found	C	H/D	N	C	H/D	N	
$MnCl_2(py)$	White	27.9	27.6	29.3	2.5	6.8	29.4	2.5	7.0	9
$MnCl_2(py\text{-}d_5)$	White	28.6	28.0	28.6	4.8	6.7	28.4	4.8	6.8	c
$MnBr_2(py)$	White	21.2	21.2	20.4	1.7	4.8	19.9	1.8	4.7	9
$MnBr_2(py\text{-}d_5)$	White	22.0	22.2	20.1	3.4	4.7	20.5	3.5	4.6	c
$CoCl_2(py)$	Lilac	27.5	27.5	28.7	2.4	6.7	28.6	2.3	7.2	6, 11
$CoCl_2(py\text{-}d_5)$	Lilac	28.2	28.0	28.1	4.7	6.6	29.3	5.2	6.5	c
$NiCl_2(py)$	Yellow	27.5	27.2	28.8	2.4	6.7	29.1	2.4	6.6	4, 5, 7, 8, 11, 12
$NiCl_2(py\text{-}d_5)$	Yellow	28.2	28.3	28.1	4.7	6.6	28.6	4.7	6.6	c
$NiBr_2(py)$	Orange	21.0	20.9	20.2	1.7	4.7	20.2	1.7	4.6	7, 8, 12
$NiBr_2(py\text{-}d_5)$	Orange	21.7	22.1	19.8	3.3	4.6	19.8	3.2	4.1	c
$CdCl_2(py)$	White	23.2	22.6	22.9	1.9	5.4	22.9	1.9	5.3	10
$CdCl_2(py\text{-}d_5)$	White	23.9	21.7	22.5	3.7	5.2	23.0	3.8	5.5	c
$CdBr_2(py)$	White	18.4	18.0	17.1	1.4	4.0	17.6	1.3	3.9	10
$CdBr_2(py\text{-}d_5)$	White	19.1	18.6	16.9	2.8	3.9	16.9	2.8	3.9	c

[a] Throughout this paper, (py) = pyridine, C_5H_5N; (py-d_5) = pentadeuteriopyridine, C_5D_5N. [b] From heating the corresponding $MX_2(py)_2$ complex. [c] New compound.

TABLE II. Far-infrared Assignments (cm^{-1}) for 1:1 Complexes of Metal Dichlorides with Pyridine.[a]

Band	Assignment[b]	$MnCl_2$ (pyridine)			$CoCl_2$(pyridine)			$NiCl_2$(pyridine)			$CdCl_2$(pyridine)		
		ν_H	ν_D	ν_H/ν_D	ν_H	ν_D	ν_H/ν_D	ν_H	ν_D	ν_H/ν_D	ν_H	ν_D	ν_H/ν_D
A	ν(MCl)	262s	262s	1.00	264ms	264ms	1.00	281s	281s	1.00	233m	232m	1.00
B	ν(MCl)	230m	232m	0.99[c]	245ms	245ms	1.00	256s	256s	1.00	216ms	216m	1.00
C	ν(MCl)	215m	214m	1.00	229m	228m	1.00	241m	240m	1.00	188msh	188msh	1.00
D	ν(MCl)	199s	199s	1.00	200s	200s	1.00	223s	221s	1.01	177s	179s	0.99[c]
		160m	160m	1.00							150m	151w	0.99[c]
E	ν(MN)		152w	1.05	182m	173m	1.05	202m	195m	1.04		143m	1.05
					176m	176sh	1.00	187m	185m	1.01	119sh	118w	1.01
		128s	126s	1.02	149m	144m	1.03	168w	165m	1.02	108s	109sh	0.99[c]
F	ν(MN)	118sh	113mw	1.04	135mw	130w	1.04	158mw	152w	1.04		104s	1.04
								146w	143w	1.02			
G	Lattice?[d]	82mw	80mw	1.03	82w	80w	1.03	78mw	75mw	1.04	80w	76w	1.05

[a] Wavenumber values given are those obtained at *ca.* 30 K as the spectra were significantly improved by cooling. Data obtained at room temperature are available on request. s = strong, m = medium, w = weak, sh = shoulder. [b] The description ν(MCl) has been used simply for convenience. [c] Ratios less than 1.00 arise from uncertainties in true band positions due to band overlap. [d] See text.

complex. Representative far-infrared spectra are shown in Figs. 1 and 2, and the assignments made are given in Tables II–IV.

Infrared Spectra

The most characteristic feature of the infrared spectra is the appearance of four high-wavenumber bands (labelled A–D) which are at lower wavenumbers for the bromides (where known) than for the corresponding chlorides by an amount given by ν(bromide)/ν(chloride) ≅ 0.82. This ratio is comparable to that found [1, 15] for the 1:2 series $MX_2(py)_2$ [(py) = pyridine] and implies that the origin of the bands is in vibrations involving appreciable motion of the halide groups. A convenient designation is 'ν(MX)', recognising that for halogen-bridged structures (as these must surely be, see below) the actual atomic motions must be more

TABLE III. Far-infrared Assignments (cm^{-1}) for 1:1 Complexes of Metal Dibromides with Pyridine.[a]

Band	Assignment[b]	$MnBr_2$(pyridine)			$NiBr_2$(pyridine)			$CdBr_2$(pyridine)		
		ν_H	ν_D	ν_H/ν_D	ν_H	ν_D	ν_H/ν_D	ν_H	ν_D	ν_H/ν_D
A	ν(MBr)	226ms	225m	1.00	248ms	244ms	1.02	179sh		
B	ν(MBr)	205m	204ms	1.00	230s	228s	1.01	173s	172s	1.01
C	ν(MBr)	176sh	172sh	1.02				147m	146m	1.01
E	ν(MN)	161s	153s	1.05	177msh	169m	1.05		140m	1.05
D	ν(MBr)	150msh		0.98[c]	188s	186s	1.01	128s	127s	1.01
					163mw	163sh	1.00			
F	ν(MN)	118m	114m	1.04	152m	147m	1.03	109ms	106ms	1.03
		95w[e]	93w[e]	1.02	135m	135m	1.00	90w	89w	1.01
		88m	86mw	1.02	110w	109w	1.01	78mw	78m	1.00
G	Lattice?[d]	64mw	62w	1.03	69mw	68m	1.01	60w	59w	1.02
								52w	52w	1.00

[a,b,c,d] See footnotes to Table II. [e] Value at *ca.* 100 K (not clearly identified at *ca.* 30 K).

TABLE IV. Raman Spectral Data for MX_2(pyridine) Complexes.[a]

Compound[b]		ν(MX)/cm^{-1}				ν(MN)/cm^{-1}	Others/cm^{-1}						
$MnCl_2$(py)	ν_H	248	201	177		119	137	94	60				
$MnCl_2$(py-d_5)	ν_D	245	199	176		114	136	93	58				
	ν_H/ν_D	1.01	1.01	1.01		1.04	1.01	1.01	1.02				
$MnBr_2$(py)	ν_H	211	192	147		123	135	70	35				
$MnBr_2$(py-d_5)	ν_D	212	191	145		118	135	69	33				
	ν_H/ν_D	1.00	1.01	1.01		1.04	1.00	1.01	1.06				
$CoCl_2$(py)	ν_H	244	239	215	196	133	153	101	68	55			
$CoCl_2$(py-d_5)	ν_D	241	234	211	193	129	147	99	65	53			
	ν_H/ν_D	1.02	1.02	1.02	1.02	1.03	1.04	1.02	1.05	1.04			
$NiCl_2$(py)	ν_H	266	245	212	176	154	141	106	91	83	75	59	37
$NiCl_2$(py-d_5)	ν_D	263	243	211	172	148	141	103	92	82	74	58	37
	ν_H/ν_D	1.01	1.01	1.00	1.02	1.04	1.00	1.03	0.99[c]	1.01	1.01	1.02	1.00
$CdCl_2$(py)	ν_H	221	180	158	145	110	79	60	37				
$CdCl_2$(py-d_5)	ν_D	221	179	–[d]	147	105	77	58	39				
	ν_H/ν_D	1.00	1.01	–	0.99[c]	1.05	1.03	1.03	0.95[c]				
$CdBr_2$(py)	ν_H	175	140	127		110	67	31					
$CdBr_2$(py-d_5)	ν_D	172	143	127		107	66	29					
	ν_H/ν_D	1.02	0.98[c]	1.00		1.03	1.02	1.07					

[a] Wavenumber values given are those obtained at *ca.* 300 K. s = strong, m = medium, w = weak, sh = shoulder. [b] Satisfactory data could not be obtained for $NiBr_2$(py) or $NiBr_2$(py-d_5). [c] Ratios less than 1.00 arise from uncertainties in true band positions due to band overlap or poor quality of the spectra. [d] Assumed overlapped by 147 cm^{-1} band.

complex than simple bond stretching. In agreement with these assignments, it is found that the bands A–D are not significantly shifted by the replacement of pyridine by pentadeuteriopyridine.

In general, two infrared bands above 100 cm^{-1} in each spectrum show appreciable deuteriation shifts ($\nu_H/\nu_D \geqslant 1.03$) and are thus attributable to modes involving motion of the pyridine groups, since internal modes of these ligands all occur at wavenumbers greater than 350 cm^{-1}. These bands (labelled E and F) are not significantly shifted when chlorine is replaced by bromine in the complexes [$NiBr_2$(py) is discussed below], so in these cases there is little coupling with the ν(MX) modes. It

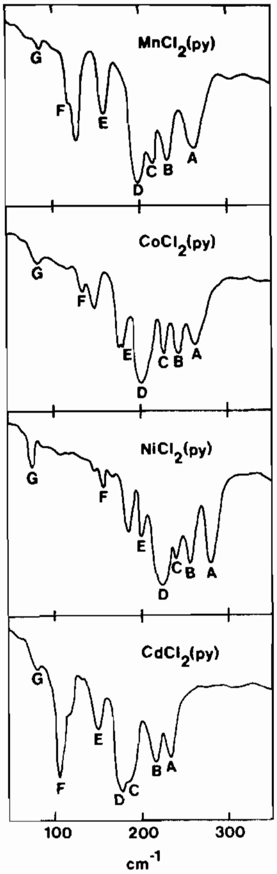

Fig. 1. Far-infrared spectra of MCl_2(pyridine) complexes at *ca.* 30 K (M = Mn, Co, Ni or Cd). The assignments for bands A–G are given in Table II and are discussed in the Text.

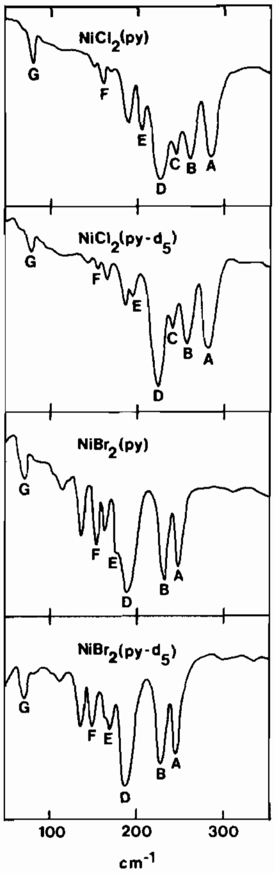

Fig. 2. Far-infrared spectra of NiX_2(pyridine) and NiX_2-(pyridine-d_5) at *ca.* 30 K (X = Cl or Br). The assignments for bands A–G are given in Tables II and III and are discussed in the Text.

should be noted that the absence of a significant deuteriation shift cannot of itself be held in evidence against assignment to a ν(MN) or similar mode, since the relative motions of the various pyridine groups must be considered [16].

We attribute both E and F to ν(MN) modes. The alternative of assigning E to ν(MN) and F to δ(NMX) may confidently be discounted because the separation between the two bands is only 25–56 cm^{-1} in the various cases. We note also that this separation is comparable to the spread of ν(MN) modes in the analogous $MX_2(py)_2$ complexes, *viz.* 21–53 cm^{-1} [1, 15]. It is recognised that these assignments place ν(MN) as low as 108 cm^{-1} [in $CdCl_2(py)$], but as discussed below this is fully compatible with the relatively high values for ν(MX).

All six bands A–F show the same variation in position with change in the metal:

$$\mathrm{Cd} < \mathrm{Mn} < \mathrm{Co} < \mathrm{Ni}.$$

The position of cadmium in this series is understandable in view of its much larger mass, while the trend involving the other three metals may be correlated with changes in the crystal field stabilization energy. Such variations have been found for metal–ligand vibrations in other systems [17–19] and lend further support to the present assignments.

A further band (labelled G) which is significantly deuteriation sensitive ($\nu_H/\nu_D \cong 1.03$) is found in each case at very low wavenumbers (56–72 cm^{-1} at 300 K), but this band shows in addition a marked dependence on the halogen, comparable to that of the ν(MX) modes [ν(bromide)/ν(chloride) = 0.75–0.91]. There is a slight variation with the metal, but a very pronounced temperature dependence on the band positions, with shifts in the range 5–17% to higher wavenumbers on cooling from 300 to *ca.* 30 K. These are all features expected on a lattice mode, and we are tempted to make such an assignment, although the positions are remarkably high for such motion in these heavy polymeric systems.

Up to three other bands are found in the spectra, in the region between E and G. These are generally of low intensity and do not all correlate readily through the series. They show deuteriation shifts of

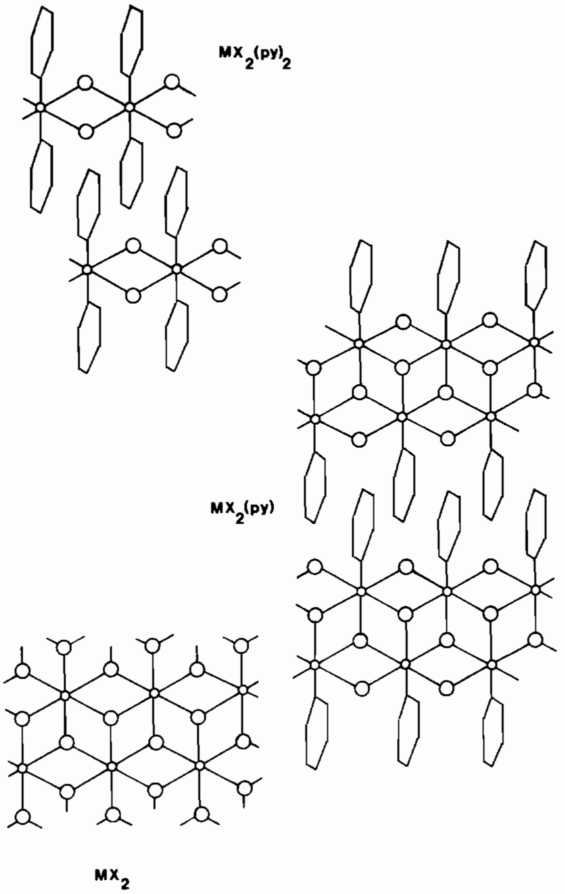

Fig. 3. Relationships between the structures of the compounds MX_2, $MX_2(py)$ and $MX_2(py)_2$ (M = Mn, Co, Ni or Cd; X = Cl or Br).

0–5 cm^{-1} (ν_H/ν_D = 1.00–1.03), and are likely to comprise δ(NMX) and δ(MX) modes, although those at higher wavenumbers may involve ν(MN).

In summary, a consistent interpretation of the spectra is that they contain four bands (A–D) assignable as ν(MX), two ν(MN) bands (E and F), one band having the characteristics of a lattice mode (G), and two or three other bands of more complex origin.

Raman Spectra

The quality of the Raman spectra obtained in the low-frequency region was not high, mainly because of the thermal instability of the compounds and (in some cases) their colour. No reliable data could be obtained for $NiBr_2(py)$. However, using analogous criteria as adopted for the infrared spectra, assignments of ν(MX) and ν(MN) modes have been made as given in Table IV. We note that three or four ν(MX) modes and one ν(MN) mode can be identified in each spectrum, at positions compatible with these assignments and close to (but not generally coincident with) the corresponding infrared bands.

Discussion

The Mn, Co and Ni complexes studied in the present work have electronic spectra and magnetic moments which clearly demonstrate that the metal atoms are octahedrally co-ordinated [4–9]. As the (py) ligands can only be unidentate, the structures must thus be polymeric with the bridging halide groups having an average coordination number of 2.5. Evidently, each metal atom has an environment of one nitrogen and five halide groups, and the double-strand chain structure shown in Fig. 3 is clearly indicated. This structure has been suggested previously for some $MX_2(py)$ compounds [4, 5], and is analogous to that found for salts $A[HgX_3]$ and $A[CdX_3]$, where A is an alkali metal cation [20], in which the terminal X^- ligand is replaced by a pyridine group. The arrangement may be considered as intermediate between the structures of the single-strand chains in the $MX_2(py)_2$ series and the infinite two-dimensional sheets in the parent MX_2 compounds, as illustrated in Fig. 3.

The close similarity of all the spectra obtained (*e.g.* Fig. 1) strongly suggests that all the compounds studied are of the same structure [$NiBr_2(py)$ is further commented upon below]. This includes the cadmium compounds, for which measurement of electronic spectra and magnetic properties are not informative. Analogous structures have been established for the related complexes $CdCl_2$(MeNHCONHMe) [21] and $CdCl_2$(imidazole) [22].

An interpretation of the spectra may be given in terms of the double-strand chain structure proposed. The appropriate approach to adopt is in terms of the line group symmetry [16], and initially we consider an isolated chain and take the (py) groups as point masses. The line group is then isomorphous with point group C_{2h}, leading to:

$$\Gamma_{\text{vib}} = 7a_g(\text{Ra}) + 4b_g(\text{Ra}) + 3a_u(\text{ir}) + 6b_u(\text{ir}).$$

Taking internal co-ordinates, we find that these eleven Raman-active and nine infrared-active modes contain:

$$\Gamma[\nu(\text{MX})] = 3a_g(\text{Ra}) + 2b_g(\text{Ra}) + 2a_u(\text{ir}) + 3b_u(\text{ir})$$

and

$$\Gamma[\nu(\text{MN})] = a_g(\text{Ra}) + b_u(\text{ir}).$$

The observation of 3–4 infrared bands and a similar number of *different* Raman bands attributable to ν(MX) modes is thus seen as fully consistent with the line group analysis for ν(MX), recognising that the band crowding in these parts of the spectra is likely to give rise to some band concealment.

The observation of two ν(MN) bands in the infrared spectra appears, at first sight, to be in contradic-

TABLE V. Comparison of ν(MX) and ν(MN) Infrared Assignments (cm^{-1}) for Metal Dihalides and their Pyridine Complexes MX$_2$(pyridine)$_2$ and MX$_2$(pyridine).[a]

M	X	Mode	MX$_2$	MX$_2$(py)[b]	MX$_2$(py)$_2$
Mn	Cl	ν(MX)	180, 230 [25]	199–262	140–175 [1, 23]
		ν(MN)	–	118, 160	214, 230 [1, 23]
Mn	Br	ν(MX)	[c]	150–226	135 [1, 23]
		ν(MN)	–	118, 161	175, 212 [1, 23]
Co	Cl	ν(MX)	190, 235 [25]	200–264	167–188 [1]
		ν(MN)	–	135, 182	227, 235, 245 [1]
Ni	Cl	ν(MX)	231, 288 [12]	223–281	154–193 [1, 23]
		ν(MN)	–	158, 202	237, 247, 262 [1, 23]
Ni	Br	ν(MX)	225 [12]	188–248	147 [1, 23]
		ν(MN)	–	152, 177	200, 240, 255 [1, 23]
Cd	Cl	ν(MX)	164, 210 [25]	177–233	127–170 [15]
		ν(MN)	–	108, 150	199 [15]
Cd	Br	ν(MX)	102, 161 [25]	128–179	105 [15]
		ν(MN)	–	109, 147	167, 180 [15]

[a] All values refer to data obtained at ambient temperature. [b] Data from present study. [c] No data available.

tion to the predictions based on the double-strand chain structure. However, an entirely analogous situation was found for the 1:2 series MX$_2$(py)$_2$ for which the crystal structures had been firmly established (for one member at least) [1, 16]. The origin of the apparent anomaly lies in the simplifications inherent in the aforementioned vibrational predictions, particularly the approximation of taking (py) as a point mass. Thus in α-CoCl$_2$(py)$_2$ the inclination of the (py) rings to the chain axis lowers the line group symmetry from D_{2h} to C_2, thereby activating the otherwise infrared-inactive symmetrical ν(MN) mode [1, 16]. The structure proposed for the MX$_2$(py) complexes studied in the present work (Fig. 3) is similarly expected to result in loss of the centre of symmetry if the (py) ring orientations are taken into account. Thus the appearance of two ν(MN) bands in the infrared spectra is not unexpected.

By the same token, both ν(MN) modes are expected to be active in the Raman spectra. That both are not found is again analogous to the situation obtaining in the MX$_2$(py)$_2$ complexes [23]. Furthermore, it is notable that the position of the one ν(MN) mode found in the Raman spectrum of each MX$_2$(py) complex is close to but not coincident with the corresponding infrared band (comparing data obtained at the same temperature). This same effect arose with the MX$_2$(py)$_2$ series, and is due to correlation field splitting [1, 16]. Evidently, the same effect is operative in the 1:1 complexes herein considered, and is compatible with the results of X-ray powder diffraction studies carried out [11] on CoCl$_2$(py) and NiCl$_2$(py).

It is tempting to seek to confirm the ν(MN) assignments by quantitative consideration of the shifts of the bands on deuteriation of the organic ligand. However, as previously pointed out [16] there are dangers in doing this. Using a simple linear symmetrical L–M–L model, the deuteriation ratio (ν_H/ν_D) for the symmetric stretching mode may be calculated [24] as 1.03 (independent of mass of M), whereas for the antisymmetric counterpart ν_H/ν_D is 1.01 using the relative atomic mass of M of Mn, Co, Ni or Cd, or 1.03 taking the [MX$_n$] framework to be infinite mass. The observed ratios are generally higher than these values (particularly for band E, 1.05), but since (especially for E) no other assignments are realistic, these data simply serve to show that the ν(MN) motions involved are more complex than may be described by the triatomic model.

The effect of the pyridine ring orientations on the ν(MN) spectral activities is not found on the ν(MX) modes. This is not surprising because the M–X bands are one step further removed from the influence; the same situation obtained for the MX$_2$(py)$_2$ complexes [1].

Two further aspects of the spectra lend strong support for the double-strand chain structure depicted in Fig. 3. Firstly, the number of infrared bands observed [making allowance for the effect on ν(MN) noted above and including band G] is 8 or 9, in almost perfect agreement with the line group prediction for the proposed structure. The agreement between the number of observed (6–12) and predicted (11) Raman modes is less satisfactory because of the poor quality of the spectral data and because some of the very low frequency bands (<50 cm^{-1}) could be lattice modes.

Secondly, it should be noted that the infrared wavenumber positions of the ν(MX) modes are comparable with the infrared values of ν(MX) in the parent (uncomplexed) dihalides MX_2 (Table V). This is consistent with the structural relationships between the two series illustrated in Fig. 3; the replacement of one halogen atom in the co-ordination sphere of the metal in MX_2 by the weaker pyridine donor compensates for the lower co-ordination number of half of the remaining halogen atoms. In agreement with this interpretation we note (Table V) that the ν(MN) band positions are at considerably lower wavenumbers than in the $MX_2(py)_2$ series, as the stronger metal–halogen bonding would weaken the M–(py) bonds (Pauling's electroneutrality principle).

Thus the vibrational spectral data provide compelling evidence that the complexes MX_2(py) have double strand halogen-bridged chain structures as depicted in Fig. 3. This conclusion applies to all the complexes studied, but the infrared spectrum of $NiBr_2$(py) is slightly unusual in that only three ν(MX) modes could be identified (Fig. 2) and, more significantly, the highest wavenumber ν(MN) mode (band E) is anomalously low compared with that in $NiCl_2$(py). We attribute this not to a grossly different structural type, because the general features are clearly closely similar to those of the other complexes studied, but to some slight distortion, possibly akin to that recently reported for $CdCl_2(CH_3CSNH_2)$ [26].

Experimental

All the complexes were prepared from the corresponding 1:2 adducts by heating on a Stanton HT-SM thermobalance in a stream of nitrogen, under conditions determined by preliminary measurements on the thermobalance. The analytical data are in Table I. Far-infrared spectra were obtained using a Beckman-RIIC FS-520, with the samples as pressed discs in polyethene (BDH Ltd.). Spectra were computed to a resolution of 5 cm^{-1}. A CTi model 20 cryocooler was used to obtain the low temperature data, with the samples estimated to be at *ca.* 30 K. Raman spectra were recorded using a Cary model 82 spectrometer with Ar^+/Kr^+ laser excitation (488.0, 514.5, 568.2, or 647.1 nm).

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