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Vibrational Spectra of some Bis(aniline) Complexes of Metal Dihalides having Planar or Octahedral Halogen-Bridged Chain Structures

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Far-infrared spectra (30–400 cm^{-1}) have been studied for a series of complexes MX_2(aniline)$_2$ where M = Mn, Ni, Cu or Cd, and X = Cl or Br. For the cadmium series, Raman spectra could also be obtained. Assignments for ν(MX) and ν(MN) modes have been made, as well as for some skeletal deformations, by noting shifts in the band positions on replacing the aniline ligand by its perdeuteriate $C_6D_5ND_2$. The results clearly show that the Mn, Ni and Cd complexes comprise octahedral polymeric halogen-bridged chains. The spectra of the Cu analogues, on the other hand, show no indication of such polymeric nature, but can very adequately be interpreted in terms of a planar monomeric structure. For both structural types, more bands are found than are predicted for the simple models normally adopted. Likely causes, related to ligand orientation and crystal field effects, are discussed. The study has clarified particularly the position of ν(MN) is these systems.

Introduction

Complexes of metal salts with aromatic amines such as aniline and its derivatives have been known for many years, and the physical properties of the simpler compounds are often used as model data for more complicated systems, for example those of biological importance. It is therefore crucial that these model data are themselves reliable, yet in the field of vibrational spectroscopy this is generally not the case. Some years ago it occurred to us that the extant literature data [1–6] on ν(MX) and ν(MN) assignments for metal dihalide complexes were lacking in consistency, and moreover (as acknowledged by some of the early authors) were individually far from substantiated. We therefore undertook a study [7] of selected complexes of this type in order to establish more reliably the metal–ligand mode assignments. In the interim [8, 9] and subsequently [10, 11], four further reports appeared relevant to this work, and these are included in the summary given as Table I [1–6, 8, 9, 11–16]. Despite the more recent work, several problems still remain:

(a) Except in the case of $ZnCl_2$(aniline)$_2$, and by inference other tetrahedral complexes, the numbers of metal–ligand bands observed, and their positions, have not properly been rationalised in terms of the structures of the complexes.

(b) Apart from relatively minor (but in some respects still quite worrying) variations in wavenumbers observed for corresponding bands by different authors, there is at least one instance of gross discrepancy, *viz.* the ν(MN) assignments for CdI_2(aniline)$_2$ [4, 6].

(c) Assignments given as ν(MN) for *p*-toluidine complexes MCl_2(*p*-toluidine)$_2$ [8] are not entirely consistent with those for $M(NCS)_2$(*p*-toluidine)$_2$ [10], even though ^{15}N substitution and the same laboratory was involved in both cases.

(d) The data on the *p*-toluidine complexes also cast doubt on many of the ν(MN) assignments for the aniline complexes, in that for the latter much lower values for ν(MN) have been included.

(e) There appears to be a dependence of ν(MN) on co-ordination geometry, which requires substantiation.

In order to help clarify some of these points, particularly (a) and (d), we report herein our results on the species MX_2(aniline)$_2$ [M = Mn, Ni, Cu or Cd; X = Cl or Br]. Our results, summarised in Tables II–IV, are more reliable than those reported hitherto for these compounds because we have covered a much extended spectral range, cooled the samples to improve the spectral quality, and employed substitution of aniline for the perdeuteriated analogue to help identify the ν(MN) bands. We have also obtained Raman spectral data, although only for the cadmium complexes, for the first time.

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TABLE I. Summary of Literature Data on the Far-Infrared Spectra of Metal Dihalide Complexes of Aniline and its Derivatives.

Complex[a]	Structure	ν(MN)/cm^{-1}	ν(MX)/cm^{-1}	Reference	Limit of study (cm^{-1})
$\mathrm{MnCl_2(An)_2}$	Octahedral polymeric[b]	374,386	227	[4]	200
		370–450[c]	318	[2]	280
$\mathrm{MnCl_2(R_nAn)_2}$	Octahedral polymeric[b]	366–397[d]	227–233[e]	[3]	200
$\mathrm{MnBr_2(An)_2}$	Octahedral polymeric[b]	350,367	n.o.[f]	[4]	200
$\mathrm{MnBr_2(R_nAn)_2}$	Octahedral polymeric[b]	360–410[d]	n.o.[f]	[3]	200
$\mathrm{MnI_2(An)_2}$	Octahedral polymeric[b]	355, 361	n.o.[f]	[4]	200
$\mathrm{CoCl_2(An)_2}$	Tetrahedral[b]	366,415	299,318	[4]	200
		370–450[c]	297,319	[2]	280
		[g]	144,235,301,316	[1]	100
		365,413	295,320	[9]	200
$\mathrm{CoCl_2(\mathit{p}\text{-}MeAn)_2}$	Tetrahedral[h]	426[i]	n.a.[f]	[8][j]	200
$\mathrm{CoCl_2(R_nAn)_2}$	Tetrahedral[b,h]	387–424[d]	292–325[k]	[3]	200
$\mathrm{CoBr_2(An)_2}$	Tetrahedral[b]	358,412	245	[4]	200
$\mathrm{CoBr_2(R_nAn)_2}$	Tetrahedral[b]	377–424[d]	238–247[e]	[3]	200
$\mathrm{CoI_2(An)_2}$	Tetrahedral[b]	349,410	*ca.* 208	[4]	200
$\mathrm{CoI_2(R_nAn)_2}$	Tetrahedral[b,h]	379–431[d]	n.o.[f]	[3]	200
$\mathrm{NiCl_2(An)_2}$	Octahedral polymeric[b]	350,377,388	238	[4]	200
		390	348	[9]	200
$\mathrm{NiCl_2(\mathit{p}\text{-}MeAn)_2}$	Octahedral polymeric[b]	414[i]	n.a.[f]	[8][j]	200
$\mathrm{NiCl_2(R_nAn)_2}$	Octahedral polymeric[b]	347–417[d]	224–238[e]	[3]	200
$\mathrm{NiBr_2(An)_2}$	Octahedral polymeric[b]	354,370,386	n.o.[f]	[4]	200
$\mathrm{NiBr_2(R_nAn)_2}$	Octahedral polymeric[b]	349–413[l]	n.o.[f]	[3]	200
$\mathrm{NiI_2(An)_2}$	Octahedral polymeric[b]	345,361	n.o.[f]	[4]	200
$\mathrm{CuCl_2(An)_2}$	Tetragonal[m]	357,430	306	[4]	200
		370–450[c]	306	[2]	280
		[g]	143, 238, 308	[1]	100
		430	355	[9]	200
$\mathrm{CuCl_2(\mathit{p}\text{-}MeAn)_2}$	[n]	445[i]	n.a.[f]	[8][j]	200
$\mathrm{CuCl_2(R_nAn)_2}$	Tetragonal[b,m]	384–425[d]	282–336[o]	[3]	200
$\mathrm{CuBr_2(An)_2}$	Tetragonal[m]	348,424	233	[4]	200
$\mathrm{CuBr_2(R_nAn)_2}$	Tetragonal[b,m]	380–425[d]	222–239[e]	[3]	200
$\mathrm{ZnCl_2(An)_2}$	Tetrahedral[m]	362,402	294	[4]	200
		370–450[c]	287, 295	[2]	280
		[g]	143,225,301	[1]	100
		363,400	285,295	[9]	200
		366,406	273,298	[11][j]	50
$\mathrm{ZnCl_2(\mathit{p}\text{-}MeAn)_2}$	Tetrahedral[h]	423[h]	n.a.[f]	[8][j]	200

(Continued on facing page)

TABLE I. *(Continued)*

$ZnCl_2(ClAn)_2$	Tetrahedral[m]	391–420[k]	298–308[p]	[5]	200
$ZnCl_2(R_nAn)_2$	Tetrahedral[h,m]	357–417[d]	285–315[p]	[3]	200
$ZnBr_2(An)_2$	Tetrahedral[m]	355, 400	230	[4]	200
$ZnBr_2(ClAn)_2$	Tetrahedral[m]	381–426[o]	232–234[e]	[5]	200
$ZnBr_2(R_nAn)_2$	Tetrahedral[m]	348–411[d]	227–256[e]	[3]	200
$ZnI_2(An)_2$	Tetrahedral[q]	342, 396	n.o.[f]	[4]	200
$ZnI_2(R_nAn)_2$	Tetrahedral[q]	346–420[d]	n.o.[f]	[3]	200
$CdCl_2(An)_2$	Octahedral polymeric[r]	351, 377	n.o.[f]	[4]	200
$CdCl_2(R_nAn)_2$	Octahedral polymeric[r]	358–403[d]	n.o.[f]	[3]	200
$CdBr_2(An)_2$	[s]	350, 365	n.o.[f]	[4]	200
$CdBr_2(R_nAn)_2$	[s,h]	350–397[d]	n.o.[f]	[3]	200
$CdI_2(An)_2$	Octahedral polymeric[q]	339, 370	n.o.[f]	[4]	200
	Tetrahedral[h]	197, 210[t]	140, 155[t]	[6]	20
$CdI_2(R_nAn)_2$	[s]	345–383[d]	n.o.[f]	[3]	200

[a] (An) = aniline, $C_6H_5NH_2$; (R_nAn) = methyl or dimethyl derivative of aniline; (ClAn) = *m* or *p*-chloroaniline. [b] Structure deduced from study of electronic spectrum. [c] This range (covering also Pd and Pt complexes) was thought possibly to embrace ν(MN) modes. [d] One or two bands in this range said most likely to be ν(MN). [e] One band in this range so assigned. [f] n.o. = not observed as below limit of study; n.a. = not assigned but within limits of study. [g] Authors unable to separate ν(MN). [h] The structures of the following compounds have been fully determined by X-ray diffraction studies: $CoCl_2(p\text{-}MeC_6H_4NH_2)_2$ [12], $CoI_2(p\text{-}MeC_6H_4NH_2)_2$ [13], $ZnCl_2(p\text{-}MeC_6H_4NH_2)_2$ [14], $CdBr_2(m\text{-}BrC_6H_4NH_2)_2$ [15], and $CdI_2(An)_2$ [16]. [i] Two additional bands (at 475–488 and 525–535 cm^{-1}) said possibly to be coupled ν(MN) modes. [j] Isotopic substitution in the ligand used as an aid to assignment. [k] Two bands in this range so assigned. [l] Up to three bands in this range said most likely to be ν(MN). [m] Structure deduced from ν(MX) positions. [n] Said to be planar or tetragonal. [o] Two or three bands in this range so assigned. [p] One or two bands in this range so assigned. [q] Structure assumed by analogy with chloro- and bromo-analogues. [r] Structure deduced by absence of ν(MX) bands in the region studied (200 cm^{-1} limit). [s] Not possible to deduce structure. [t] Values obtained at *ca.* 100 K.

Results and Assignments

The observed data for the complexes chosen for study are listed in Tables II–IV; representative spectra are shown in Figs. 1 and 2.

The most striking aspect of the results obtained is the close similarity of the spectra of the Mn, Ni and Cd complexes, with the spectra of the Cu series being markedly different. The general appearance, in comparison with data obtained on model systems (see also Table I), provides convincing evidence that the Mn, Ni and Cd compounds comprise linear polymeric chains in which octahedrally co-ordinated metal atoms are linked by halide bridges. On the other hand, the copper complexes are either tetragonal or planar (see Discussion).

Infrared Spectra of Octahedral Complexes (M = Mn, Ni and Cd)

Assignments have been made by noting: (i) the positions of internal modes of the ligand, (ii) bands principally dependent on the halogen, (iii) bands which undergo substantial shift on substitution of $C_6H_5NH_2$ by $C_6D_5ND_2$, and (iv) the variation in band position with changing metal in the isostructural series formed by Mn, Ni and Cd.

The first problem thus encountered is the identification of bands arising from internal vibrations of the aniline ligand itself, and distinguishing these from ν(MN) modes in particular. This is a problem recognised by other authors [2–4, 10, 11] but which has not, in our view, adequately been resolved for octahedral complexes at least. The region of particular difficulty is 300–400 cm^{-1} in the Mn, Ni and Cd complexes. A system of 2–4 bands of medium-strong intensity is observed, giving the appearance of two doublets (identified as A and B in Fig. 1) which are not always resolved. Each doublet shows analogous variation in the series as follows.

(a) A shift to lower wavenumbers on ligand deuteriation, with $\nu_H/\nu_D \simeq 1.04$. For a linear triatomic model L–M–L, treating the aniline ligand L as a point mass, the ratio ν_H/ν_D for both the symmetric stretch ν_s(MN) and the antisymmetric stretch ν_a(MN) [assuming the $(MX_2)_n$ chain to be of infinite mass] may be calculated [17] as 1.04.

TABLE II. Far-Infrared Assignments (cm^{-1}) for MX_2(aniline)$_2$ Complexes having Octahedral Polymeric Halogen-bridged

Band	Assignment[b]	$MnCl_2$(aniline)$_2$			$MnBr_2$(aniline)$_2$		
		ν_H	ν_D	ν_H/ν_D	ν_H	ν_D	ν_H/ν_D
A	ν(MN)	388sh			384sh?	374sh?	1.05
		384ms	368ms	1.04	375ms	362ms	1.04
B	ν(MN)	325m	314m	1.04	332ms	323ms	1.03
		311mw	302sh	1.03	325ms	314m	1.04
					257mw[c]	245w[c]	1.05
C	ν(MX)	244sh					
		233s	232s	1.00	162s	159s	1.02
		216m	218m	0.99[d]	152s	150s	1.01
			212sh				
D	δ(NMN)	204s	197s	1.04	206s	198s	1.04
		190s	185m	1.03	199s	188s	1.06
E	ν(MX)	164m	162m	1.01	122ms	120ms	1.02
		155sh	154sh	1.01			
		144m	143m	1.01	100s	99s	1.01
		116ms	118ms	0.98[d]	89sh	89sh	1.00
		96mw			79sh	78sh	1.01

[a] Wavenumber values given are those obtained at *ca.* 30 K as the spectra were significantly improved by cooling. Data obtained refer to band positions in the $C_6H_5NH_2$ and $C_6D_5ND_2$ complexes, respectively. A question mark indicates that the presence of unknown. [d] Ratios less than 1.00 arise from uncertainties in true band position due to overlap.

TABLE III. Raman Assignments (cm^{-1}) for CdX_2(aniline)$_2$ Complexes[a].

Assignment[b]	$CdCl_2$(aniline)$_2$	$CdBr_2$(aniline)$_2$[c]		
		ν_H	ν_D	ν_H/ν_D
ν(CdN)	374wbr	374wbr	358vw	1.04
	324wbr	324mw	315mw	1.03
ν(CdX)	210ms	131m	132mbr	0.99[d]
		106mw	104w	1.02
ν(NCdN)	194s	184s	176ms	1.05
		82mw	82w	1.00
		68s	67s	1.01

[a] Data obtained at room temperature. s = strong, m = medium, w = weak, br = broad, m = medium, v = very. [b] The description ν(MX) is used simply for convenience. [c] ν_H and ν_D refer to band positions in the $C_6H_5NH_2$ and $C_6D_5ND_2$ complexes, respectively. [d] A ratio of less than 1.00 arises from uncertainties in true band positions due to fluorescence.

TABLE IV. Far-infrared Assignments (cm^{-1}) for CuX_2-(aniline)$_2$ Complexes[a].

Assignment[b]	$CuCl_2$(aniline)$_2$	$CuBr_2$(aniline)$_2$		
		ν_H	ν_D	ν_H/ν_D
c		384w	316w?	1.22
ν(CuN) b_{2u}	361s	354s	340s	1.04
ν(CuX) b_{3u}	313vs	242vs[d]	243s	1.00
δ(NCuN) b_{3u}	242s	242vs[d]	227ms	1.07
π(NCuN) b_{1u}	175ms	166ms	160ms	1.04
c	169sh	152w	148w	1.03
δ(XCuX) b_{2u}	145ms	123ms	121ms	1.02
c	122sh	110w	104wbr	1.06
π(XCuX) b_{1u}	109s	82s	80s	1.02
c		54mw	51w	1.06

[a] See footnote to Table II. [b] Symmetry labels are based on a D_{2h} point group model. [c] See text. [d] Coincident bands.

(b) Variation with the metal in the order: Mn < Ni > Cd. This order is that expected for a metal–ligand stretching mode on the basis of crystal field stabilisation energy effects (Mn < Ni) and the substantially heavier mass of Cd, and has been found for many related systems [18–20]. These trends, of themselves, are strong pointers towards assigning *all* the bands observed in this range

Structures.^{a}

NiCl$_2$(aniline)$_2$			NiBr$_2$(aniline)$_2$			CdCl$_2$(aniline)$_2$	CdBr$_2$(aniline)$_2$		
ν_H	ν_D	ν_H/ν_D	ν_H	ν_D	ν_H/ν_D	ν_H	ν_H	ν_D	ν_H/ν_D
397ms	380s	1.04	395ms	378ms	1.04	386m	373ms	359ms	1.04
384ms	372sh	1.03	378ms	365ms	1.04	378m			
352ms	339ms	1.04	359ms	345m	1.04	328ms	324ms	311ms	1.04
343sh	330sh	1.04	349ms	336m	1.04	311ms			
253s	250s	1.01	188s	186s	1.01	223sh	140sbr	139sbr	1.01
237m	235m	1.01	179s	177s	1.01	208sbr			
220s	214s	1.03	224ms	214m	1.05	191s	192m	181sh	1.06
205m	198m	1.04	208s	201s	1.03	183m	181s	172ms	1.05
180w	178w	1.01	150s	147s	1.02	153mbr	111ms	109ms	1.02
173m	170mw	1.02							
						134m	83ms	81ms	1.02
155vw	153w	1.01				123w			
						105sh			
145ms	143ms	1.01	133ms	129ms	1.03	95sbr	73ms	71ms	1.03
			121sh	119sh?	1.02				
133w	130sh?	1.02	107mw	102mw	1.05				
92w?			78s	75ms	1.04				
						52w	39vw	37vw	1.05

at room temperature are available on request. s = strong, m = medium, w = weak, br = broad, sh = shoulder, v = very. ν_H and ν_D
the band is not certain. ^{b}The description ν(MX) is used simply for convenience. ^{c}Not observed at room temperature; origin

as ν(MN). Such assignment differs to some extent from previous suggestions [2–4, 10, 11] and implies that the weak 390 cm^{-1} band found in the spectrum of aniline itself [21], which we have been unable to confirm, is either of vanishingly low intensity in the present series of complexes or is significantly shifted to higher wavenumbers (where a number of weak bands appear to be located). However, we believe that the trends noted above provide relatively convincing evidence for our assignments of ν(MN) presented in Table II.

One other internal mode of aniline is expected in the spectral region under study, namely, a substituent-sensitive mode of the aromatic ring, found in the Raman spectrum of the free ligand at 233 cm^{-1} [21]. Whereas this band has been assigned [11] at 205, 225 cm^{-1} in the spectrum of ZnCl$_2$(aniline)$_2$ [described as γ(ring)], it is not apparent in the spectra of M(NCS)$_2$(aniline)$_2$ species (M = Co, Ni, Cu or Zn) [10], nor (at least above 200 cm^{-1}) in the spectra of halide complexes studied by others [3, 4, 6]. In the present work we can find no evidence for this band, since although the chlorides studied do show absorption in the required range, these bands are unequivocally ν(MCl) as described below.

At considerably lower wavenumber than the ν(MN) range, at 180–225 cm^{-1}, another doublet (D) is found in each spectrum (splitting of 7–16 cm^{-1}) which shows a substantial deuteriation shift: $\nu_H/\nu_D \simeq 1.04$. These bands are clearly too low in wavenumber to be ν(MN). For example, in the closely related octahedral MX$_2$(pyridine)$_2$ series (M = Mn, Fe, Co, Ni or Cd), the spread of ν(MN) is only 21–56 cm^{-1} [6, 22] compared with a spread of 177–203 cm^{-1} between doublets A and D in the present case. The positions of bands D are, however, compatible with assignments to metal–nitrogen deformation modes. On the basis of a simple model in which only the aniline ligand moves, the (MX$_2$)$_n$ chain being taken as being of infinite mass, the deuteriation ratio ν_H/ν_D for a δ(NMN) mode may be calculated [17] to be 1.04, in agreement with the present observations. Furthermore, we note that for the structurally related NiX$_2$(NH$_3$)$_2$ complexes (X = Cl, Br or I), a δ(NMN) mode has been located at 180–210 cm^{-1} [22], in agreement with earlier predictions [23], close to the δ(NMN) assignments now made for the aniline series. Thus we confidently attribute the doublet D to δ(NMN).

A prominent pair of bands (C) is found in the spectra of the chlorides at 208–253 cm^{-1} which is insignificantly affected by deuteriation ($\Delta\nu \leqslant 3$ cm^{-1}, with ν_H/ν_D generally 1.00–1.01) but which is at substantially lower wavenumbers in corresponding

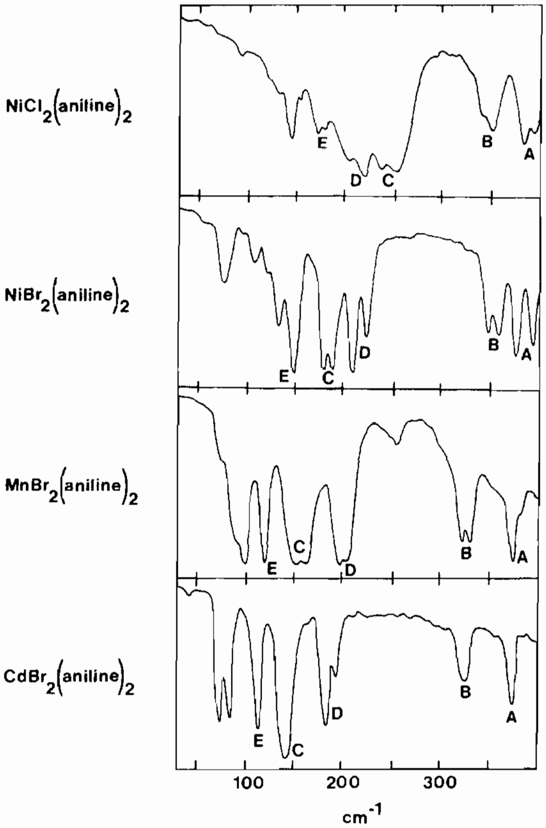

Fig. 1. Far-infrared spectra of some $MX_2(aniline)_2$ complexes at *ca.* 30 K. The assignments for bands A–E are given in Table II and are discussed in the Text: A and B, $\nu(MN)$; C and E, $\nu(MX)$; D, $\delta(NMN)$.

bromides. The ratio ν_{Br}/ν_{Cl} is *ca.* 0.72, which firmly establishes the bands as being predominantly $\nu(MX)$ modes, recognising that for the polymeric halogen-bridged chain structures of these compounds this description is an approximate one [22]. Indeed, the positions of bands C are entirely consistent with the $\nu(MX)$ assignment for $[MX_2L_2]_n$ octahedral chain structures such as the bis(pyridine) analogues [22]. We note also that bands C vary with the metal in the order expected for the $\nu(MX)$ modes: Mn < Ni > Cd.

At lower wavenumbers than features A–D are found a number of bands which are not all easily correlated within the series. Where such correlation can be made with confidence, shifts with changing the halogen atom are observed which are indicative of vibrations involving appreciable motion of the halogen atoms. For example, ν_{Br}/ν_{Cl} = 0.70–0.87 for bands designated E in Table II and Fig. 1; these are found towards the lower end of the region previously reported for $\nu(MX)$ in the analogous $MX_2(pyridine)_2$ and $MX_2(pyrazine)$ series [6, 24], and we are thus inclined to the view that these are probably reasonably described as $\nu(MX)$ modes. They show the expected variation with M: Mn < Ni > Cd.

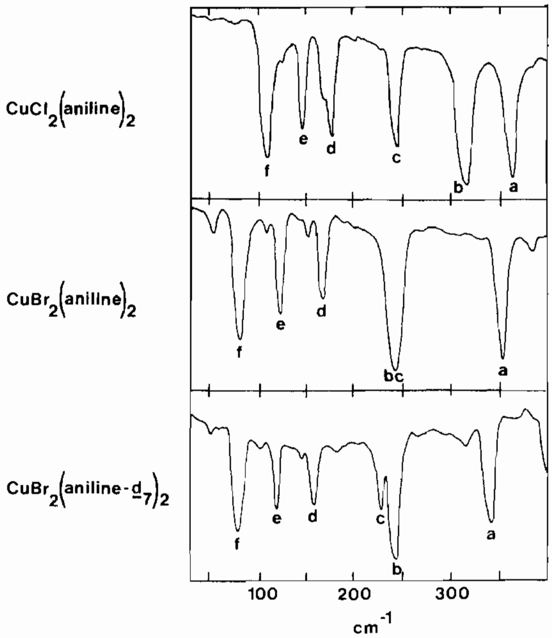

Fig. 2. Far-infrared spectra of $CuX_2(aniline)_2$ complexes at *ca.* 30 K. Band assignments are given in Table IV and are discussed in the Text: a, $\nu(CuN)$; b, $\nu(CuX)$; c, $\delta(NCuN)$; d, $\pi(NCuN)$; e, $\delta(XCuX)$; f, $\pi(XCuX)$.

The other low frequency bands cannot be more precisely defined than skeletal deformations.

Copper(II) Complexes

As indicated previously, we find that the spectra of these complexes are characteristic of tetragonally distorted or planar structures, in keeping with earlier conclusions [4], so are appropriately considered separately.

The correlation of bands from the chloride to the bromide may be made in a very straightforward manner, since the spectra are simpler and the bands are less crowded together than in the octahedral complexes (Fig. 2). The only initial problem was confirming the apparent merging of the 242 and 313 cm^{-1} bands of the chloride into a single feature at 242 cm^{-1} in the bromide, but this ambiguity was clearly resolved (Fig. 2) by comparison with the spectrum of $CuBr_2(aniline\text{-}d_7)_2$. The assignments given in Table IV, made on the basis of halogen- and deuteriation-dependence, together with the vibrational analysis (see Discussion) show quite distinctly the presence of one $\nu(CuN)$ and one $\nu(CuX)$ mode for each complex.

Raman spectra

Only for the cadmium compounds prepared could reliable Raman spectra be obtained in the region of interest. With such limited data, the assignments made must be viewed with caution, but our proposals

(Table III) appear to complement the infrared results. Raman lines in comparable positions and with similar deuteriation behaviour to the infrared bands are found and are analogously assigned.

Discussion

Octahedral Complexes (M = Mn, Ni and Cd)

All the available evidence (Table I and the present work) points towards the Mn, Ni and Cd complexes having halogen-bridged polymeric chain structures in which the metal atoms are octahedrally co-ordinated. As with the corresponding $MX_2(pyridine)_2$ complexes, therefore, the appropriate starting point for consideration of their vibrational spectra is a line group analysis [25]. Taking the organic ligands as point masses the line group is isomorphous with point group D_{2h}, leading to:

$$\Gamma_{vib} = 2a_g(Ra) + b_{1g}(Ra) + b_{2g}(Ra) + b_{3g}(Ra) + 2b_{1u}(ir) + 2b_{2u}(ir) + 2b_{3u}(ir).$$

Using internal co-ordinates we find:

$$\Gamma[\nu(MX)] = a_g(Ra) + b_g(Ra) + b_{1u}(ir) + b_{3u}(ir)$$

and

$$\Gamma[\nu(MN)] = a_g(Ra) + b_{2u}(ir).$$

Thus six infrared-active fundamentals are predicted containing two $\nu(MX)$ modes (really in-plane deformations of the $[MX_2]_n$ chains) and one $\nu(MN)$ mode (antisymmetric stretching). Very clearly, and irrespective of any incertainties in precise assignments, the number of bands observed in the infrared spectra is substantially in excess of these predictions, and we must therefore consider likely causes.

If the full geometry of co-ordinated aniline is included in the model (rather than the point mass approximation as used above), this introduces not only internal modes of the ligand (the appearance of which, in this spectral region, we have discounted earlier in this paper) but also vibrational modes of the complex which originate from loss of rotational freedom of the isolated ligand, *e.g.* torsional motion about the M–N bond. However, such effects cannot be the complete explanation of the current problem because the number of additional modes thus predicted (three) is still insufficient to account for the number of bands observed.

On the other hand, the three-dimensional nature of the aniline groups will imply a particular ligand orientation, so that the line group symmetry may not be as used in the vibrational analysis above. A doubling of the length of the repeat unit of the chain by taking such orientation into account gives quite good agreement between the number of infrared-active skeletal modes predicted (10 or 12 depending on the detailed model) and observed (9–14, generally 13). However, in order to explain the multiplicity in the $\nu(MN)$ bands it is necessary also for the chain symmetry to be non-centrosymmetric. Unless the aniline ligands adopt random or quite irregular orientations, *i.e.* for all reasonably predictable isolated chain structures, the centres of symmetry will be retained along a chain, so we are led to believe that the origin of the band multiplicity is in the effect of low site symmetry for the chains. A similar situation obtained in the analogous complexes $MX_2(pyridine)_2$, for which the pyridine ring orientation is known (for one member of the series at least), where it was further necessary to invoke correlation field splitting [22, 25]. While there is no direct evidence for correlation splitting in the present case, other than analogy with the bis(pyridine) complexes, such an effect would very elegantly explain the observed $\nu(MN)$ splitting. Study of the Raman spectra could, in principle, help to clarify the position, but the obtainable data are too limited to afford the desired confidence. Further, the $\nu(MN)$ bands observed in the Raman (Table III) are not well defined, and this does not allow a reliable $\nu(MN)$ Raman band count to be made. It is, though, clearly evident that an acceptable interpretation of the number of bands observed in the infrared spectra requires consideration of a non-centrosymmetric site symmetry and/or a unit cell analysis involving correlation field splitting.

Copper(II) Complexes

As the spectra obtained are clearly incompatible with the predictions made for a halogen-bridged chain polymer, but are indicative of a planar (or considerably tetragonally distorted) structure, we consider first a point group approach. Taking the aniline ligands as point masses, the planar *trans*-$[CuX_2L_2]$ unit is of D_{2h} symmetry, so that:

$$\Gamma_{vib} = 2a_g(Ra) + b_{1g}(Ra) + 2b_{1u}(ir) + 2b_{2u}(ir) + 2b_{3u}(ir),$$

of which:

$$\Gamma[\nu(CuX)] = a_g(Ra) + b_{3u}(ir)$$

and

$$\Gamma[\nu(CuN)] = a_g(Ra) + b_{2u}(ir).$$

Thus one $\nu(CuX)$ and one $\nu(CuN)$ mode will be infrared-active. The other four infrared bands expected comprise in-plane deformations $\delta(XCuX)$ $[b_{2u}]$ and $\delta(NCuN)$ $[b_{3u}]$, and out-of-plane modes $\pi(XCuX)$ $[b_{1u}]$ and $\pi(NCuN)$ $[b_{1u}]$.

The observation of six prominent bands in the spectrum of each complex (Fig. 2), allowing for the coincidence of two bands in the case of $CuBr_2(aniline)_2$ as described above, is thus fully consistent with this vibrational analysis. Moreover, the assignments (Table IV), which are readily made by noting deuteriation- and halogen-dependence of the band positions, show the expected number of modes of each vibrational type.

However, closer scrutiny of the spectra obtained at low temperatures shows the presence of additional, weak absorption bands which cannot be accounted for using the simple point group approach above. The 'extra' bands are at 169 and 122 cm^{-1} in the chloride, and at 152, 110 and 54 cm^{-1} in the bromide. For reasons analogous to those put forward in the case of the octahedral complexes, we discount possible attribution to internal modes of the aniline ligands*. There thus seem to be two plausible explanations for the origin of the additional bands. Firstly, they might arise from torsion or rocking motions about the Cu–N bonds (such motions are not considered in the point ligand mass model used above). The observed frequencies seem to be on the high side for such modes (except possibly the 54 cm^{-1} band), but such explanation cannot be excluded particularly because the bands show substantial deuteriation shifts [ν_H/ν_D = 1.03–1.06 (only the bromide so studied)] and a relatively small halogen-dependence (ν_{Br}/ν_{Cl} = 0.90). The second possible explanation to consider is that effects are operating analogous to those indicated in the polymeric octahedral series, *viz.* lowering of symmetry due to ligand orientations and/or crystal field effects. However, there is no perceptible splitting of the ν(CuN) and ν(CuX) bands, whereas these would be expected to be the most susceptible to such effects (*cf.* present work and related systems [18, 22, 25]); we therefore doubt this alternative explanation.

The spectra of the copper(II) complexes may thus be fully understood in terms of a monomeric structure having a *trans*-planar skeleton. If there is any longer Cu...X bonding of crystallographic significance, it is not apparent in the spectra in the same way as in CuX$_2$(pyridine)$_2$ and related systems [26].

Conclusions

This work has highlighted some of the problems which arise when seeking to make far-infrared spectral assignments even for model compounds of reasonably authenticated structure, and has illustrated the types of considerations which need to be made in solving such problems. The dangers in adopting too simple a model for predicting the number of skeletal fundamentals is evident from both structural types studied. It is now fairly clear that for the present series of octahedral polymers at least,

TABLE V. Comparison of ν(MX) and ν(MN) Infrared Assignments (cm^{-1}) for Metal Dihalide Complexes of some Related Nitrogen-donor Ligands^a.

M	X	Mode	MX$_2$(NH$_3$)$_2$	MX$_2$(pyridine)$_2$	MX$_2$(N$_2$H$_4$)$_2$	MX$_2$(aniline)$_2$^{b}
Mn	Cl	ν(MX)	c	140–175 [22, 24]	210^d [28]	152, 161, 222
		ν(MN)	c	214, 230 [22, 24]	342 [28]	324, 374
Mn	Br	ν(MX)	c	135 [22, 24]	175^d [28]	118, 148, 158
		ν(MN)	c	175, 212 [22, 24]	341 [28]	327, 371, 384
Ni	Cl	ν(MX)	187^e [22]	154–193 [22, 24]	c	169, 177, 230, 247
		ν(MN)	435 [23]	237, 247, 262 [22, 24]	409 [29]	347, 378, 390
Ni	Br	ν(MX)	140, 160^e [22]	147 [22, 24]	c	145, 179
		ν(MN)	434 [23]	200, 240, 255 [22, 24]	c	348, 358, 372, 387
Cd	Cl	ν(MX)	215 [23]	127–170 [6]	c	150, 214
		ν(MN)	375 [23]	199 [6]	338 [29]	310, 373, 376
Cd	Br	ν(MX)	c	105 [6]	c	108, 137
		ν(MN)	368 [23]	167, 180 [6]	c	319, 369
Cu	Cl	ν(MX)	267^f [23]	229, 287 [27]	c	308
		ν(MN)	480^f [23]	266 [27]	440 [29]	358
Cu	Br	ν(MX)	218^f [23]	204, 256 [27]	c	235
		ν(MN)	488^f [23]	268 [27]	c	350

^{a}Except where indicated, all values refer to measurements at room temperature, hence the differences between data for MX$_2$(aniline)$_2$ in this Table and in Tables II and IV. ^{b}Results from present study. ^{c}No data available. ^{d}M–X bonds are terminal in these complexes. ^{e}Values obtained at *ca.* 100 K. ^{f}α-crystalline forms.

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*There is some indication of a possible weak band at 384 cm^{-1} in the spectrum of CuBr$_2$(aniline)$_2$, shifting to 316 cm^{-1} in the deuteriate (ν_H/ν_D = 1.22), which could conceivably correspond to the internal mode reported at 390 cm^{-1} for free aniline [21].

crystal field effects are as important as for the bis(pyridine) analogues [25], particularly in respect of the $\nu(MX)$ and $\nu(MN)$ modes.

The position of $\nu(MN)$ in these systems now seems fairly well established. It is noteworthy that for MX_2L_2 systems the $\nu(M{-}NH_2C_6H_5)$ bands occur at wavenumbers intermediate between those for $\nu(M{-}NH_3)$ [22, 23] and $\nu(M{-}NC_5H_5)$ [6, 22, 24, 26, 27], and tend to be in a similar region to $\nu(MN)$ in the hydrazine complexes $MX_2(N_2H_4)_2$ [28, 29], showing the influence of both bond type and ligand mass (Table V).

It is also now clear that the earlier assignments for $CdI_2(aniline)_2$ [6] are in error, and that at least one of the two bands observed in the 340–390 cm^{-1} range (now found at 341, 377 cm^{-1} at room temperature, and at 347, 386 cm^{-1} at *ca.* 30 K) must be $\nu(CdN)$.

Experimental

All the aniline complexes studied in the present work have been described previously and were prepared similarly [4]. The perdeuteriates were obtained by analogous procedures. All the compouds reported herein gave satisfactory elemental analytical data. Far-infrared spectra were obtained using a Beckman-RIIC FS-520 interferometer, to a resolution of 5 cm^{-1}. The samples were studied as pressed discs in polyethene (BDH Ltd.) cooled to *ca.* 30 K using a CTi model 20 closed-cycle helium cryocooler. Raman spectra were obtained on a Cary 81 instrument with 568.2 nm (Ar^+/Kr^+) laser excitation.

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