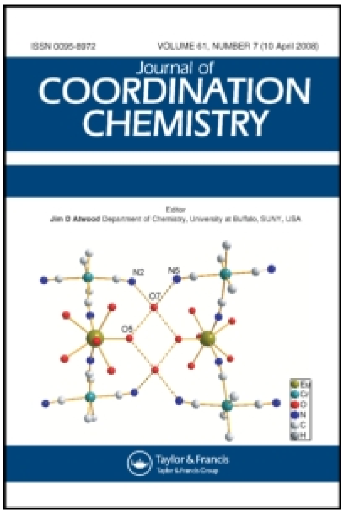

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COMPLEXES OF 8-AMINOOUINOLINE. II*. THE INFRARED SPECTRA OF THE BIS- AND MONO(AMINOQUINOLINE) COMPLEXES OF METAL(II) HALIDES

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The infrared spectra of the complexes $M(aq)_2(H_2O)_2X_2$ (M = Fe, Co, Ni, Cu; aq = 8-aminoquinoline; X = Cl, Br) have been determined over the range 4000–50 cm^{-1}. Absence of νM–X bands indicates that the halide is not coordinated to the metal ion and the complexes are correctly formulated $[M(aq)_2(H_2O)_2]X_2$. Deuteration of the amino group and the effects of metal ion substitution enable assignment of the $\nu M-NH_2$, νM–N and $\nu M-OH_2$ modes as well as the amino group vibrations. ^{18}O-Labelling assists in identifying the νO–H, νO–H·····X and δO–H bands. The spectra are consistent with *trans*-octahedral coordination and axial bonding of the water molecules. The far infrared spectra of the *mono*(aminoquinoline) complexes $[M(aq)X_2]_n$ (M = Cu, Zn; X = Cl, Br) are consistent with the proposed structure of polymeric octahedral coordination involving both bridging and terminal M–X bonds. The $\nu M-NH_2$, νM–N, νM–X(terminal) and νM–X(bridging) bands are assigned by studying the effects of amino group deuteration, metal ion substitution and halide substitution.

Keywords: 8-Aminoquinoline, complexes, first row, zinc, infrared spectra, isotopic labelling

INTRODUCTION

There is considerable diversity of composition and structure among the metal(II) complexes of 8-aminoquinoline (aq).[1] Apart from the *tris*(aq) complexes $[M(aq)_3]^{2+}$ which were discussed in Part I, *bis* and *mono*(aq) complexes of formula $M(aq)_2(H_2O)_2X_2$ and $[M(aq)X_2]_n$ (X = Cl, Br) have been reported. None of these complexes has received crystallographic attention but this study will reveal the extent to which infrared spectroscopy may assist in elucidating their probable molecular structures.

EXPERIMENTAL

The cobalt, nickel and copper complexes of formula $[M(aq)_2(H_2O)_2]X_2$ were prepared by previously reported methods.[2,3] The iron complex was synthesized by the addition of an aqueous solution of iron(II) chloride to an ethanolic solution of aq in a 2.5 : 1 molar ratio. The red suspension was stirred for 0.5 hr and filtered to remove the complex which was washed with ethanol and dried over silica gel overnight under reduced pressure. The corresponding bromo complex could not be

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*Part I: preceding paper in this issue. † Author for correspondence.

prepared by this method. The deuterated nickel and copper complexes were prepared as reported for the unlabelled compound except that EtOD and D_2O were substituted for ethanol and water. The complex $[Ni(aq)_2(^{18}OH_2)_2]Br_2$ was prepared as described for the unlabelled compound except that H_2O was replaced by $^{18}OH_2$.

The *mono*(aq) complexes $[M(aq)X_2]_n$ were prepared as previously reported[4,5] for X = Cl; the bromides were prepared as follows. A methanolic solution of aq was added to an aqueous solution of the anhydrous metal bromide in a 1 : 1 molar ratio. The precipitate which formed after a few minutes was stirred for 0.5 hr and collected by filtration. It was washed with methanol and dried over silica gel under reduced pressure. The deuterated zinc complex was prepared using the appropriate deuterated solvents. The purity and sources of the labelled compounds were as follows: EtOD (99.8%, Aldrich), MeOD (99.0% Merck-Frosst), D_2O (99.7%, Merck-Frosst) and $^{18}OH_2$ (90.0%, Alfa). Analytical data are shown in Table I.

TABLE I
Analytical data for metal(II) complexes of 8-aminoquinoline.

	Calculated			Found		
Complex	%C	%H	%N	%C	%H	%N
$Fe(aq)_2(H_2O)_2Cl_2$	47.92	4.47	12.42	47.60	4.47	12.30
$Co(aq)_2(H_2O)_2Cl_2$	47.59	4.43	12.33	47.40	4.25	12.20
$Ni(aq)_2(H_2O)_2Cl_2$	47.62	4.44	12.34	47.45	4.20	12.25
$Cu(aq)_2(H_2O)_2Cl_2$	47.12	4.39	12.21	47.05	4.25	12.15
$Cu(aq\text{-}d_2)_2(D_2O)_2Cl_2$	46.31	4.32	12.00	47.00	4.40	12.15
$Co(aq)_2(H_2O)_2Br_2$	39.80	3.71	10.31	39.80	3.80	10.30
$Ni(aq)_2(H_2O)_2Br_2$	39.82	3.71	10.32	39.80	3.60	10.30
$Ni(aq)_2(^{18}OH_2)_2Br_2$	39.46	3.68	10.23	39.50	3.80	10.10
$Ni(aq\text{-}d_2)_2(D_2O)_2Br_2$	39.24	3.65	10.17	39.50	3.80	10.10
$Cu(aq)_2(H_2O)_2Br_2$	39.47	3.68	10.23	39.60	3.65	10.10
$Cu(aq\text{-}d_2)_2(D_2O)_2Br_2$	38.07	3.55	9.87	38.30	3.40	9.75
$Cu(aq)Cl_2$	38.80	2.89	10.05	38.80	2.85	10.05
$Zn(aq)Cl_2$	38.54	2.88	9.99	38.85	3.00	9.80
$Zn(aq\text{-}d_2)Cl_2$	38.27	2.85	9.92	37.80	2.95	9.80
$Cu(aq)Br_2$	29.41	2.19	7.62	29.25	2.20	7.45
$Zn(aq)Br_2$	29.27	2.18	7.58	28.90	2.20	7.40

The mid-IR spectra were determined on Nujol mulls (4000–180 cm^{-1}) between CsI plates and as hexachlorobutadiene mulls (3500–2000 and 1500–1300 cm^{-1}) between CsI plates on a Perkin-Elmer 983 spectrophotometer. The far-IR spectra (500–50 cm^{-1}) were determined on Nujol mulls between polyethylene plates on a Digilab FTS 16B/D interferometer.

RESULTS AND DISCUSSION

The bis*(8-aminoquinoline)*bis*(aquo) complexes* $[M(aq)_2(H_2O)_2]X_2$ *(M = Fe, Co, Ni, Cu; X = Cl, Br)*

The spectra of these complexes are depicted in Figure 1 and the frequencies are reported in Table II. Actual tracings of the spectra of the complex derived from $NiBr_2$ and its ND_2-analogue are shown in Figure 2.

TABLE II

Frequencies (cm^{-1}) and band assignments of the complexes $[M(aq)_2(H_2O)_2]X_2$ in the regions 3500–3000 and 1700–50 cm^{-1}. Shifts ≤ 1 cm^{-1} are not reported.

M = Fe	M = Co		M = Ni		M = Cu		
X = Cl	X = Cl	X = Br	X = Cl	X = Br[a]	X = Cl[a]	X = Br[a]	Assignment
n.o.[b]	3295	3289	3305	3323(831,864)[c]	3409(901)	3414(890)	νO–H
3202	3199	3197	3208	3197(802)			νN–H asym
		3151		3152(787)		3146(787)	
3098	3104	3102	3100	3104(747)[d]	3109(768)		νO–H...X
3078	3082	3078	3080	3078(709)	3062(803)	3051(787)	νN–H sym
1646	1647		1651			1651(2)	ν ring
1623	1626	1632	1627	1633(0)	1630(+8)	1631	
						1621(5)	
1591	1592	1591	1593	1592(0)	1592(0)	1593(0)	
1576	1579	1573	1580	1574(420)	1577(425)	1581(427)	NH_2 scissor
					1569		
		1527		1533(379)[e]			δO–H
1505	1504	1502	1505	1504(0)	1508(0)	1503(+6)	ring + C–H modes
1472	1474	1472	1474	1475(0)	1475(0)	1476(0)	
				1443(+4)			
1423	1424	1421	1424	1424(0)[f]	1423(0)	1425(2)	
1397	1400	1401	1401	1401(sh)	1405(+2)	1402(+5)	
					1400	1393	
1385	1389	1392	1400(sh)	1395(+5)	1382(0)	1382(0)	
				1382(0)			
1376	1375	1373	1376	1374(0)			
1316	1318	1316	1320	1318(0)	1318(0)	1319(0)	
1260	1262	1258	1262	1258(0)	1257(+2)	1255(+4)	
1244	1245	1243	1245	1244(0)	1246(0)	1247(0)	
1215	1216	1213	1216(sh)	1215(sh)[c](+10)	1216(6)	1218(7)	νC–N + αC–H
1203	1207	1204	1209	1207(2)	1206	1209	
1174	1175	1174	1177	1175(+2)	1174(+4)	1176(+2)	αC–H
1131	1132	1130	1141	1133(3)	1145(8)	1153(15)	τNH_2 + αC–H
1125	1120(sh)	1125	1133				
1076	1070	1078	1080	1078(0)	1084(4)	1085(5)	αC–H
1056	1059	1058	1062	1061(0)	1065(0)	1065(0)	
1028	1029	1028	1030	1030(+4)	1030(+3)	1030(+1)	
990	991	990	990	989(0)	989(0)	992(0)	γC–H
975	979	975	980	976(+2)	976(6)	979	
						958(+5)	
						952	

921	915						
894	898	897	900	899(2)	905(7)	906(7)	ωNH$_2$
829	829	828	829	827(4)	827(3)	828(0)	ωNH$_2$ + γC–H
807	808	807	808	808(0)	809(0)	810(0)	γC–H
789	788	787	788	786(8)^g	780(6)	782(7)	ωNH$_2$ + ν ring
775	775	771	775	771(0)	767(n.o.)^b	772(n.o.)^b	γC–H
718	718	718	719	718(+2,10)	723(9)	725(10)	
633	641	632	647	636(12)	643	647	ρNH$_2$ + γ ring
					628(9)	632(12)	
					608(26)	589(3)	ρNH$_2$
589	592	589	592	600(24)			
577		581	577	590(sh)(0)	575		ρNH$_2$ + γ ring
	557	556		560(sh)(13)			
528	537	528	542	531(0)	539	546	ρNH$_2$
496	501	494	506	496(10)	494(3)		ρNH$_2$ + γ ring
464	470	465	463		463(+2)	462(+2)	γ ring
					425(0)	427(0)	
419	428	425	433	431(15)			νM–NH$_2$ + γ ring
370	381	381	390	390(9)	412(2)	408(4)	νM–NH$_2$
	314	322	315	324(0)			
266	272	267	285	284(1)	299(2)	297(0)	γC–N
				272(–)			
216	235	231	252	249(0)	279(0)	271(0)	νM–N(py)
					264sh(–)	264sh(–)	
(216)	220	213	234	229(2)	216(0)	211(0)	γ ring
			219sh				
180	189	198	191	206(2)	169(2)	193sh	
		175sh					
160	175	157	(191)	185(10)	183(5)	158(5)	νM–OH$_2$
138	135	130	139	138(0)^h	154sh(–)	155(7)	
103	110	100sh	115	117(9)^i	96(0)	83(0)	δL–M–L
88	99	86	104	95(0)	(96)(0)	(83)(0)	
	77	62	81	69(0)	77(0)	74(4)	Lattice + NH$_2$
55	55			55(0)	55(1)	69(0)	torsion

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[a] Values in parentheses are the shifts induced by ND$_2$- (and D$_2$O-) labelling of the complex. [b] n.o. = not observed. [c] ^{18}0 shift = 7 cm^{-1}. [d] ^{18}0 shift = 8 cm^{-1}. [e] ^{18}0 shift = 12 cm^{-1}. [f] ^{18}0 shift = 2 cm^{-1}. [g] ^{18}0 shift = 3 cm^{-1}. [h] ^{18}0 shift = 2 cm^{-1}. [i] ^{18}0 shift = 5 cm^{-1}.

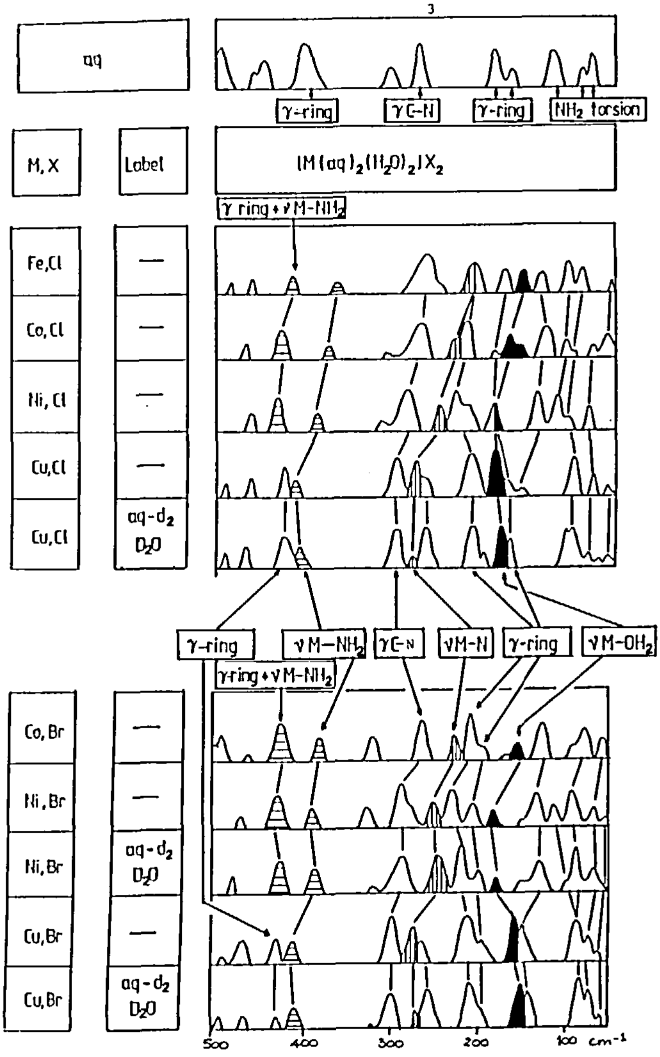

FIGURE 1 IR spectra of the complexes [M(aq)$_2$(H$_2$O)$_2$]X$_2$.

There has been no conclusive evidence in the literature as to whether water molecules or halide ions complete the octahedral stereochemistry in the complexes of this formula. From electronic spectra, Nielsen and Dahl[5] suggested that the nickel complex should be formulated [Ni(aq)$_2$(H$_2$O)$_2$]X$_2$. The i.r. spectra should reveal the presence of metal-halide stretching modes if the formulation is [M(aq)$_2$X$_2$].2H$_2$O but no vibrational study has been reported. It will be seen below that no νM–X modes are observed and we conclude that the correct formulation is [M(aq)$_2$(H$_2$O)$_2$]X$_2$. Furthermore, by observing the effects on the spectra of deuteration of the amino group and of metal ion substitution and by comparing the spectra of the complexes with that of the ligand, firm assignments of the νM–NH$_2$, νM–N and νM–OH$_2$ bands may be elicited. ^{18}*O*-Labelling of the complex did not assist with the assignment of the metal–ligand modes because the band shifts were within the limits of experimental error in the far-i.r. region. ^{18}O-Labelling did, however, assist in identifying the O–H stretching and bending modes.

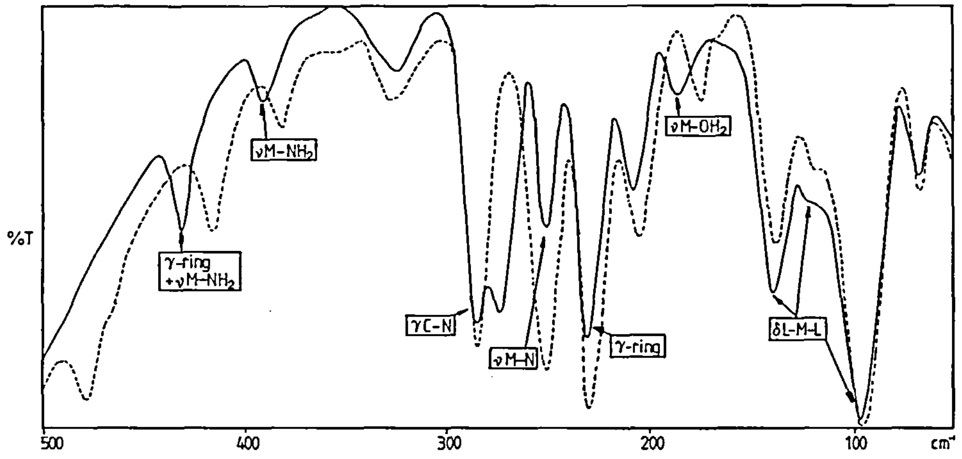

FIGURE 2 IR spectra of $[Ni(aq)_2(H_2O)_2]Br_2$(——) and $[Ni(aq\text{-}d_2)_2(D_2O)_2]Br_2$ (----) in the region 500–50 cm^{-1}.

The 4000–500 cm^{-1} Region

The vO–H bands are relatively sharp, suggesting the presence of coordinated water molecules rather than crystal water. These bands are readily detected by their sensitivity towards deuteration (Δv between 800 and 900 cm^{-1}) and towards ^{18}O-labelling (Δv = 7 cm^{-1} in the $NiBr_2$ complex). The band could not be detected in the iron complex. The O–H bending mode was only identified with certainty in the $CoBr_2$ and $NiBr_2$ complexes. In the latter, it was found to undergo a low frequency shift of 12 cm^{-1} on ^{18}O-labelling and a shift of 379 cm^{-1} on D_2O deuteration. The only other band to exhibit a significant shift on ^{18}O-labelling of the $NiBr_2$ complex occurs at 3104 cm^{-1} (Δv = 8 cm^{-1}). This observation and its high sensitivity towards deuteration suggests that it probably originates in hydrogen bonded vO–H · · · · · Br.

The NH stretches are readily identified within the range 3200–3050 cm^{-1}. Their *d*-sensitivities approximate the theoretical values calculated for deuteration of a hypothetical N–H diatomic species.[6] The NH_2 scissoring mode is readily distinguished from the neighbouring ring modes near 1600 cm^{-1} by its sensitivity towards deuteration, while the NH_2 twisting, wagging and rocking modes are similarly identified near 1150, 900–750 and 650–500 cm^{-1}, respectively. Bands near 1200 cm^{-1} are likewise assigned to vC–N. The remaining bands within the range 4000–500 cm^{-1} are assigned to the i.p. and o.o.p. ring and C–H modes by their absence of sensitivity to deuteration of the amino group and by comparison with the spectrum of 8-aminoquinoline.[1]

The 500–50 cm^{-1} region

Figure 1 depicts the spectra in this region together with the spectrum of aq itself. The latter is seen to be rich in far-i.r. bands (mainly γ ring o.o.p. bends). The γ-ring band at 400 cm^{-1} in the spectrum of aq shifts to higher frequency on coordination and becomes metal sensitive in the crystal field stabilization energy (CFSE) sequence: Fe < Co < Ni. Deuteration of the $NiBr_2$ complex reveals that the band is *d*-sensitive ($\Delta\nu = 15\,cm^{-1}$). We therefore assign this band to $\nu M{-}NH_2 + \gamma$ ring except for the copper complexes where it loses its sensitivity to deuteration and becomes a pure γ-ring band. The band within the range 370–412 cm^{-1} is assigned to a pure $\nu M{-}NH_2$ mode on the grounds of its low intensity, its *d*-sensitivity (Δν between 2 and 9 cm^{-1}) and its occurrence in a region free from ligand bands.

There is a strong band in each spectrum within the range 260–300 cm^{-1} with a low or zero *d*-sensitivity. It corresponds in position with the strong band at 267 cm^{-1} in the spectrum of 8-aminoquinoline.[1] This is assigned to the o.o.p. γC–N mode. It is in a similar position to the γC–O band of 8-hydroxyquinoline.[7]

Below the γC–N band there is a band of moderate intensity which is assigned to νM–N on the basis of its absence of sensitivity to deuteration of the amino group, its position, which is close to that of νM–N in $[M(ox)_3]$, $[Ni(ox)_2(H_2O)_2]$ and $[Ni(aq)_3](ClO_4)_2$,[1,8] its occurrence in a region free from ligand bands and its marked sensitivity to the coordinated metal ion in the sequence Fe < Co < Ni < Cu.[9] The next two bands in decreasing frequency order are relatively insensitive towards deuteration of the amino group and to substitution of the metal ion. They are accordingly assigned to the γ-ring bands which occur at 186 and 163 cm^{-1} in the free ligand spectrum.[1]

The following band in order of decreasing frequency occurs within the range 160–190 cm^{-1}. It is sensitive to ND_2 labelling (Δν between 5 and 10 cm^{-1}) and is strongly metal-sensitive in the sequence Fe < Co < Ni > Cu. This sequence is the anticipated[9] order for $\nu M{-}OH_2$ if tetragonal distortion of the copper complex involves elongation of the $Cu{-}OH_2$ bonds (as occurs in the corresponding complex of 8-hydroxyquinoline, *trans*-$[Cu(ox)_2(H_2O)_2]$).[8] All of these observations are consistent with the assignment of this band to $\nu M{-}OH_2$. The five bands within the range 160–50 cm^{-1} remain for assignment to the metal–ligand bonding modes, the NH_2 torsional modes and the lattice vibrations but there is no ready means of distinguishing between them.

In view of the large number of ligand bands within the far-i.r. region of 8-aminoquinoline, there is much vibrational coupling but we were able ultimately to identify three vibrationally pure metal–ligand stretching bands, *viz* one each for $\nu M{-}NH_2$, νM–N and $\nu M{-}OH_2$. This finding suggests that these complexes have *trans*-octahedral symmetry as has been found for the complexes $[M(ox)_2(H_2O)_2]$ from both X-ray diffraction and vibrational spectroscopic studies.[8]

The mono*(8-aminoquinoline) complexes of metal(II) halides,* $[M(aq)X_2]_n$ *(M = Cu, Zn; X = Cl, Br)*

Complexes of formula $[M(R_2\text{-}aq)X_2]$ (M = Ni, Cu; X = Cl, Br; R = Cl, Br, I) have been reported by Izquierdo *et al.*[10,18] On the basis of their electronic spectra, the compounds were assigned polymeric octahedral structures with terminal and bridging halides. As will be seen, the IR spectra are consistent with this proposal. Table 3 reports the frequencies and Figure 3 depicts the spectra. Actual tracings of the spectra of $[Cu(aq)Cl_2]_n$ and $[Cu(aq)Br_2]_n$ are shown in Figure 4.

ND_2-Labelling was applied to the complex $[Zn(aq)Cl_2]_n$. Eleven bands occur below 470 cm^{-1}. Apart from the lattice mode at 69 cm^{-1}, four of these bands (at 277,

TABLE III
Frequency data (cm^{-1}) and assignments for the complexes $[M(aq)X_2]_n$ (500–50 cm^{-1}).

M = Cu		M = Zn		
X = Cl	X = Br	X = Cl[a]	X = Br	Assignment
493	493	493(+4)	493	γ ring
462	463	463	461	
423	421	417(11)	415	$\nu M\text{-}NH_2$
405	400	395(10)	400	
335	338	321(8)	320	
306	275	277(0)	254	$\nu M\text{-}X_t$
282	253		241sh	
230	174	230(1)	172	$\nu M\text{-}X_{br}$
205	209	203(10)	207	$\nu M\text{-}N$
192	192	191(10)	191	
162	149	137(0)	86	δX-M-X
123	112	121(0)	75	
			135	δL-M-L
	99		113	
61	78	69(0)	59	lattice

[a] Values in parentheses are the ND_2-induced shifts. Shifts $\leqslant 1\ cm^{-1}$ are not reported.

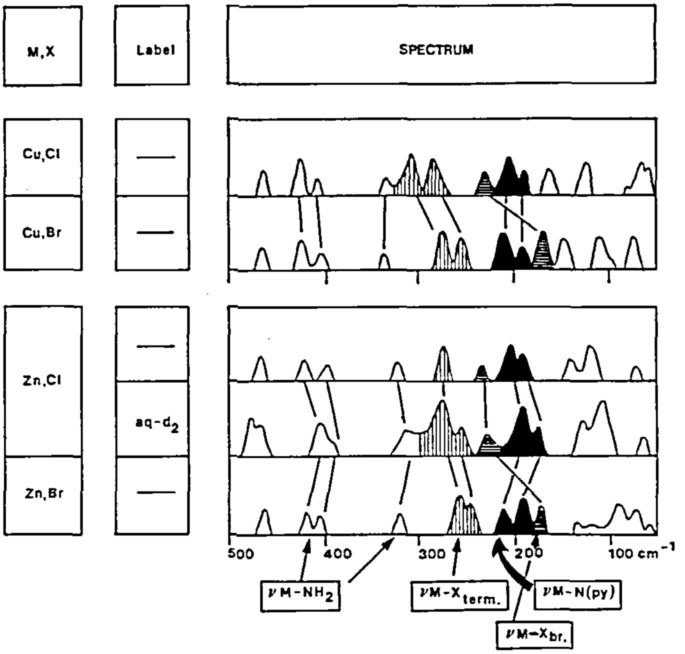

FIGURE 3 Far-IR spectra of the complexes $[M(aq)X_2]$ in the region 500–50 cm^{-1}.

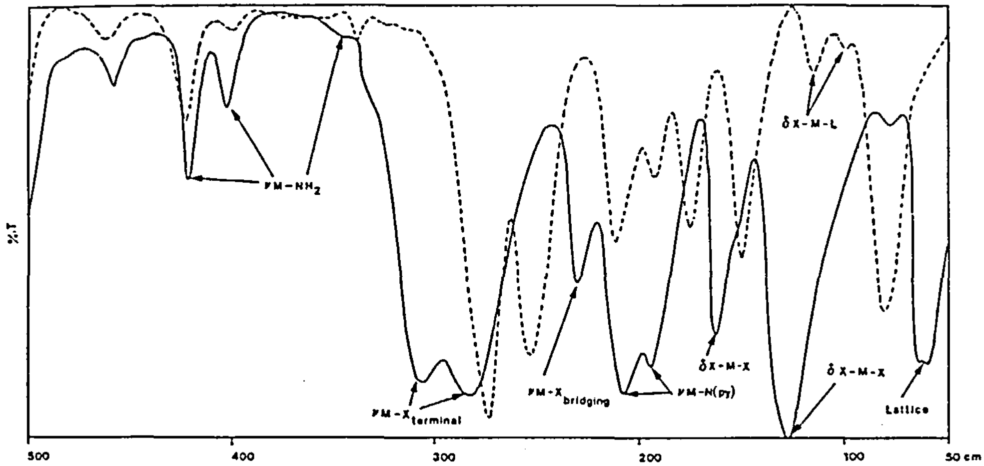

FIGURE 4 IR spectra of the complexes [$Cu(aq)Cl_2$] (——) and [$Cu(aq)Br_2$] (----) in the region 500–50 cm^{-1}.

230, 137 and 121 cm^{-1}) are unaffected by ND_2-labelling and are therefore assigned to Zn–Cl modes. This is confirmed by the substantial shifts which occur on bromide substitution. It is proposed that the first two bands are assigned to νZn–Cl_t (terminal) and νZn–Cl_{br} (bridging) modes and the last two to Cl–Zn–Cl bending vibrations. Of the remaining six bands, the group of three at 417, 395 and 321 cm^{-1}, which shift between 8 and 10 cm^{-1} on ND_2-labelling, are firmly assigned to νZn–NH_2 bands, and the bands at 203 and 191 cm^{-1} to νZn–N modes. These occur within the region reported for 8-hydroxyquinoline complexes.[8] Their sensitivity to ND_2-labelling is probably a result of vibrational coupling of νZn–N with νZn–NH_2, or a ligand mode incorporating the NH_2 group. The assignment of the δL–M–X and δL–M–L bands is difficult because these bands are generally much weaker than the δX–M–X bands and may be masked by the latter. This was indeed substantiated by the substitution of Cl by Br which causes the δX–M–X bending modes to shift to lower frequencies (Δν ~ 50 cm^{-1}), exposing the underlying δN–Zn–N and/or δN–Zn–Br bands at 135 and 113 cm^{-1}.

The assignments for the [$Cu(aq)X_2]_n$ spectra are readily made by comparison with the analogous zinc complexes. The doubling of the νCu–X stretching modes is undoubtedly associated with the tetragonal distortion (Jahn–Teller effect) which is known to occur in the copper complexes but not in the zinc chelates. The finding of three νM–MH_2 bands and two νM–N bands is not surprising when the low symmetry of these polymeric molecules is considered.

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