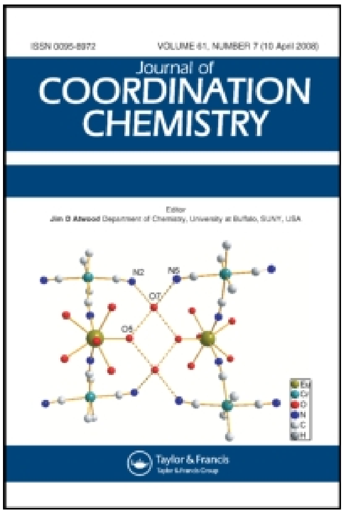

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COMPLEXES OF 8-AMINOQUINOLINE. I. THE INFRARED SPECTRA OF THE LIGAND, THE TRIS COMPLEXES OF IRON, COBALT AND NICKEL PERCHLORATES AND THEIR ND_2 ANALOGUES

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Deuteration of 8-aminoquinoline (aq) at the amino groups and comparison of the infrared spectrum of aq with those of aniline and quinoline enables reliable assignments to be proposed for the amino stretching and bending modes and the internal modes of the aminoquinoline rings. The spectra of the *tris*(8-aminoquinoline) complexes of iron, cobalt and nickel perchlorates have been examined over the range 4000–50 cm^{-1} with assignments based on the ligand study and the effects of metal ion substitution and deuteration of the nickel complex. The existence of two $\nu M–NH_2$ and two $\nu M–N(aq)$ bands is consistent with facial (*cis-cis*) octahedral coordination about the metal ion.

Keywords: 8-Aminoquinoline, infrared spectra, complexes, isotopic labelling

INTRODUCTION

There have been relatively few vibrational studies of 8-aminoquinoline (aq) and its metal complexes.[1–10] Early reports[2,4] were restricted to tentative assignments of the internal ligand modes by comparison with the established assignments for aniline and quinoline. Coakley[5] and Jensen and Nielsen[6] deuterated the ligand amino groups in order to assign the NH_2 modes but only partial D/H exchange was achieved. The infrared spectra of the structurally simple complexes $[M(aq)_3](ClO_4)_2$ have not been studied except for brief reference[3] to the spectrum of the cobalt(II) complex in which comment was restricted to the perchlorate bands. The *tris* complexes therefore seemed to be a suitable basis for a more general infrared examination of 8-aminoquinoline complexes.

EXPERIMENTAL

The iron and cobalt complexes were prepared and isolated using Schlenk tube techniques and were stored under nitrogen. The isotopic purity and sources of the labelled compounds used were EtOD: 99.8%, Aldrich and D_2O: 99.7%, Merck-Frosst.

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8-Aminoquinoline–d_2 (aq-d_2) was prepared by refluxing aq in EtOD for 3 hr. After removal of the solvent under reduced pressure, the process was repeated twice. The aq–d_2 was stored over silica gel under reduced pressure to prevent H/D exchange.

Only the cobalt *tris* complex $[Co(aq)_3]^{2+}$ has previously been reported.[3] The following general method served for the synthesis of the iron, cobalt and nickel complexes. An ethanolic solution of the hydrated metal perchlorate was added dropwise to an ethanolic solution of the ligand in a 3.5 : 1 molar ratio. After stirring (5 min), the complex was collected by filtration, washed (ethanol) and dried over silica gel overnight under reduced pressure. The nickel complex is hygroscopic and was stored in a desiccator. This method failed to produce a copper or zinc complex even with a six-fold excess of ligand.

Anal. Calcd. for $[Fe(aq)_3](ClO_4)_2.\frac{1}{2}H_2O$: C, 46.58; H, 3.62; N, 12.07%. Found: C, 46.70; H, 3.80; N, 12.20%. Calcd. for $[Co(aq)_3](ClO_4)_2.2H_2O$: C, 44.65; H, 3.89; N, 11.57%. Found: C, 44.90; H, 3.95; N, 11.35%. Calcd. for $[Ni(aq)_3](ClO_4)_2.H_2O$: C, 45.80; H, 3.70; N, 11.87%. Found: C, 45.40; H, 3.70; N, 11.65%. Calcd. for $[Ni(aq\text{-}d_2)_3](ClO_4)_2.2D_2O$: C, 45.03; H, 3.92; N, 11.67%. Found: C, 45.00; H, 3.85; N, 11.45%.

The mid-IR spectra were determined on Nujol mulls (4000–180 cm^{-1}) and as hexachlorobutadiene mulls (3500–2000 and 1500–1300 cm^{-1}) between CsI discs 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 DISCUSSIONS

The IR Spectrum of 8-Aminoquinoline

To a first approximation, the IR spectrum of aq may be regarded as a composite of those of aniline and quinoline. Comprehensive studies of the IR spectra of the latter two molecules[11,12] simplifies the comparison (Table I).

TABLE I
Infrared band assignments for 8-hydroxyquinoline based on the effects of deuteration and comparison with aniline and quinoline.

Aniline	Assignment[11]	Quinoline	Assignment[12]	8-Amino-quinoline & (d_2-shift)	Assignment
3440	νN–H asym			3450[a](867)	νN–H asym
3360	νN–H sym			3349[b](904)	νN–H sym
1618	NH_2 scissor	1619		1615[c](5)	ν ring + NH_2 scissor
1600	ν ring	1593	ν ring	1599(26)	
1586				1590sh(2)	ν ring
		1571		1566(414)	ν ring + δNH_2
1500		1500		1505(3)	ν ring
1469		1469		1470(1)	
		1431		1426(2)	
1382	comb.	1392		1394(4)	
		1371		1368(+4)	
1330	ν ring			1335[d](+1)	

TABLE I (*continued*)

Aniline	Assignment[11]	Quinoline	Assignment[12]	8-Amino-quinoline & (d_2-shift)	Assignment
1278	ν ring + νC–N			1279(+30)	ν ring + νC–N
		1256		1239(5)	
		1216		1207(3)	αC–H
1175		1192	αC–H	1183(+7)	
1118	αC–H	1118		1125(+7,19)	αC–H + τNH_2
		1095		1094(2,8)	αC–H
1028		1031		1037(7)	
		1013	ν ring	1021(−)	ν ring
984	$^{13}C^{12}C_5H_5.NH_2$	980	γC–H	985(0)	
970		970		962(0)	γC–H
960	γC–H	939		942(0)	
880				889(3)	
		867	γ ring	863(0,12)	γ ring + ωNH_2
832	γC–H			819(0)	γC–H
		786	γC–H	789(0)	γC–H + ν ring
		785	ν ring		
		760		760[e](1)	ν ring
761		741	γC–H	751(3)	γC–H
691	γ ring			703[f](1,9)	γ ring + ρNH_2
618		628	γ ring	641(0)	γ ring
				577(+4,9)	ρNH_2
527	ρNH_2	521	ν ring	545(7)	ν ring + ρNH_2
501		(505)		509(+8)	
490	2 × NH_2 torsion	479		484(0)	
		415		436(0)	γ ring
390	γ ring	392		400(2)	
			γ ring	297(−)	
				267(9)	γC–N
		193		186(1)	γ ring
		178		163(5)	
				113(1)	NH_2 torsion
				77(0)	
				68(0)	

[a] Previously reported at 3440 cm^{-1} (ref. 4) and 3450 cm^{-1} (ref. 5) and assigned to νN–H. [b] Previously reported at 3340 cm^{-1} (ref. 4) and at 3345 cm^{-1} (ref. 5) and at 3340 cm^{-1} (ref. 6) and assigned to νN–H. [c] Previously reported at 1619 cm^{-1} and assigned to NH_2 scissor (ref. 6). [d] Previously reported at 1336 cm^{-1} (ref. 2), 1330 cm^{-1} (ref. 4) and 1339 cm^{-1} (ref. 6) and assigned to νC–N. [e] Previously reported at 760 cm^{-1} and assigned to ρNH_2 (ref. 4). [f] Previously reported at 704 cm^{-1} and assigned to ρNH_2 (ref. 6).

The N–H stretching bands occur within the normal range 3500–3000 cm^{-1} and shift to the 2590–2440 cm^{-1} region on deuteration. The observed ν^D/ν^H ratio has the normal value of 0.73.[13] Residual νN–H bands remain in the deuterated spectrum as is normally observed even at high levels of deuteration. The 1700–1500 cm^{-1} region comprises the ν ring and NH_2 scissoring modes. The intense band at 1566 cm^{-1} is by far the most *d*-sensitive band; the magnitude of its d_2-shift (414 cm^{-1}) is close to the theoretical shift of a vibrationally pure NH_2 scissoring mode.[13]

Previous workers[2,4,6] have assigned the band at 1330 cm^{-1} to νC–N. We assign this band to νring because it is found to be unaffected by deuteration and is at the same position as the νring mode of aniline.[11] We have assigned the *d*-sensitive band at 1279 cm^{-1} to νC–N, possibly coupled with the ring stretch. The unexpected upward shift of this band to 1309 cm^{-1} in aq–d_2 is similar to that observed for the corresponding band in aniline–d_2[11]. The NH_2 twisting mode yields a *d*-sensitive band at 1125 cm^{-1}. The possibility exists that it is coupled with an αC–H vibration, the band at 1118 cm^{-1} in quinoline having been so assigned.[12] Similarly, the band at 863 cm^{-1} is assigned to the NH_2 wag coupled with γring.

The band at 760 cm^{-1}, previously assigned to a NH_2 rocking mode[4] is *d*-insensitive. We have therefore assigned this band to νring. In agreement with Jensen and Nielsen[6], we have assigned the *d*-sensitive band at 703 cm^{-1} to ρNH_2 coupled with γring. Several bands in the 500 cm^{-1} region are also *d*-sensitive and therefore qualify for assignment to ρNH_2, while the previously unassigned peak at 267 cm^{-1}, shifting 9 cm^{-1} to lower wavenumber on deuteration, is attributed to γC–N by analogy with the γC–O band at 266 cm^{-1} in the spectrum of 8-hydroxyquinoline.[14]

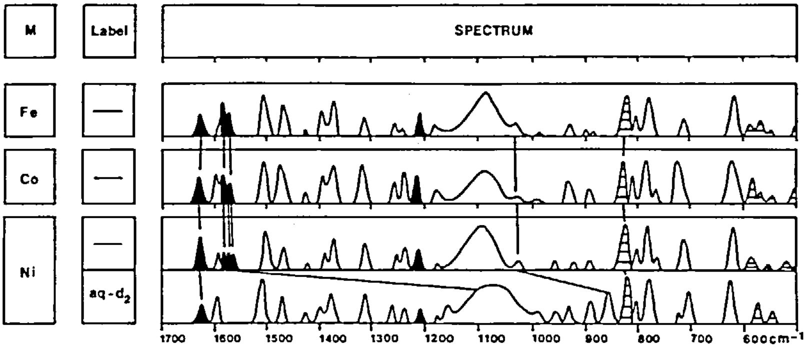

FIGURE 1 IR spectra of the complexes $[M(aq)_3]\ (ClO_4)_2$ from 1700–500 cm^{-1}. Solid linked bands: coupled NH_2 scissor; solid unlinked bands: coupled νC–N; linked bands: τNH_2; shaded linked bands: coupled ωNH_2; shaded unlinked bands: coupled ρNH_2.

The IR Spectra of the Complexes $[M(aq)_3](ClO_4)_2.xH_2O$

The mid-IR spectra are depicted in Figure 1 and the frequencies, shifts and assignments are reported in Table II. The band patterns of the unlabelled complexes are remarkably similar. The ν_3 perchlorate mode exhibits its normal broad and intense character spanning some 150 cm^{-1}, thereby obscuring certain aq modes. The IR-forbidden ν_1 band occurs weakly near 930 cm^{-1}. Both bands are, of course, unaffected by deuteration. Possible activation of ν_2 (near 460 cm^{-1}) and ν_4 (near 620 cm^{-1}) cannot be excluded because of masking by aq bands in these regions.

The internal ligand modes of aq exhibit the normal (generally upward) frequency shift on complexation. The NH_2 stretching and bending modes are readily identified by their shifts on deuteration (of the nickel complex) and the νC–N band is identified at 1214 cm^{-1}, by its *d*-sensitivity of 57 cm^{-1}.

Below 500 cm^{-1}, the spectrum of aq is relatively rich in infrared bands which renders the assignment problem of its complexes difficult (Figure 2). The magnetic

TABLE II

Frequencies (cm^{-1}) and band assignments for the complexes [M(aq)$_3$](ClO)$_4$)$_2$.

Fe	Co	Ni(aq-d_2 shift)	Assignment
3360	3299	3299(832,879)	νN-H asym
3230	3244	3248(860,913)	νN-H sym
1626	1625	1627(7)	ν ring + NH_2 scissor
1595sh	1593	1594(1)	ν ring
1582	1585	1586(429)	ν ring + NH_2 scissor
		1582(−)	
1565sh	1569	1568(~475)	NH_2 scissor
1505	1504	1506(+1)	ring + C–H modes
1470	1472	1472(+1)	
1426	1426	1426(+2)	
1396	1390	1392(+5)	
1374	1375	1375(+4)	
1314	1315	1316(0)	
1257	1259	1259(+2)	
1239	1239	1239(0)	
1209	1212	1214(7,57)	αC–H + νC–N
1179	1176	1177(+1)	αC–H
1091	1086	1091(+2)	ν_3ClO_4
1033	1028	1029(170)	τNH_2
986	989	989(0)	γC–H
		959(0)	
928	930	930)0)	ν_1ClO_4
901			γC–H
892	892	894(4)	
825	826	826(5)	γC–H + ωNH_2
808	808	808(0)	γC–H + ν ring
779	782	782(5)	ν ring + ωNH_2
	771	771(6)	γC–H
715	715	717(+1,10)	γ ring + ρNH_2
621	621	621(0)	γ ring
589	585	587(14)	γ ring + ρNH_2
567	570		
550	553	560(14)	ν ring + ρNH_2
505sh	510sh	520(73)	ρNH_2
497	499	499(3)	γ ring
466	468	467(+1)	
446			
414	418	424(23)	νM–NH_2
345	369	381(11)	
269	264	261(4)	γC–N
235	229		
196	198	209(6)	νM–N
143	148	156(+2)	
134	139		δL–M–L
81			
69	72	72(0)	lattice
65	65	65(−)	

moment of the cobalt complex (μ_{eff} = 5.10 B.M.) is typical of spin-free octahedral Co(II) chelates. The similarity of the infrared band patterns suggests that the iron, cobalt and nickel complexes are isostructural octahedral monomers which could have *facial* (C_3) or *meridional* (C_1) symmetry. The former configuration requires four vM–L modes and the latter, six. Since we observe only four such bands, *facial* symmetry is proposed for these complexes. In this respect, they resemble the *facial* (*cis–cis*) configuration of the complexes $[M(ox)_3]$ (ox = 8-hydroxyquinoline) which also yield four vM–L bands in their IR spectra.[15]

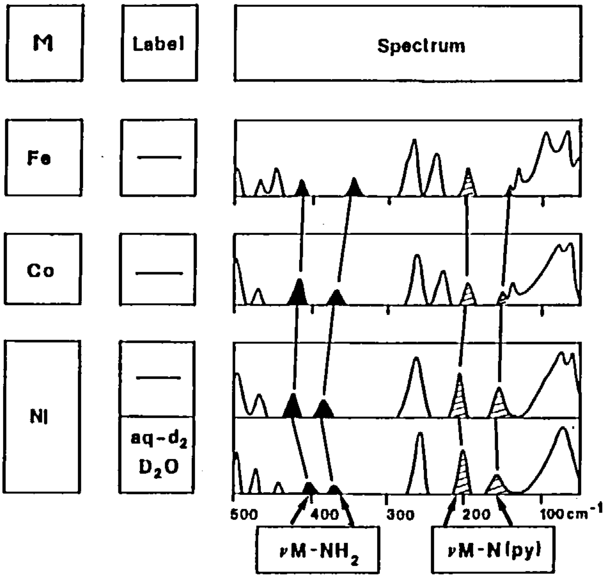

FIGURE 2 Far-IR spectra of the complexes $[M(aq)_3](ClO_4)_2$ in the region 500–50 cm^{-1}.

Reference to Figure 2 shows that there are five or six bands in the 430–140 cm^{-1} region. Two of these (near 420 and 380 cm^{-1}) are significantly sensitive to both metal ion substitution and ND_2-deuteration (Δv = 23 and 11 cm^{-1}, respectively) and are therefore assigned to vM–NH_2 modes. The bands near 210 and 160 cm^{-1} are also M-sensitive but relatively unaffected by ND_2-deuteration. These are therefore assigned to vM–N(aq) modes. The very intense band near 260 cm^{-1} corresponds in both frequency and *d*-sensitivity with the strong band at 267 cm^{-1} in the spectrum of aq where it has been assigned to γC–N mode of the ligand. Since this band is practically insensitive to metal ion substitution, it is assigned to γC–N in the spectra of the complexes also. Unfortunately, the spectra below 140 cm^{-1} are not well resolved but one of the δL–M–L bands may be distinguished in the iron and cobalt complexes at 134 and 139 cm^{-1}, respectively.

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REFERENCES

1. C.M. Harris and E.D. McKenzie, *J. Inorg. Nucl. Chem.*, **29**, 1047 (1967).
2. J.C. Fanning and L.T. Taylor, *J. Inorg. Nucl. Chem.*, **27**, 2217 (1965).
3. R. Nast, H. Bier and J. Gremm, *Z. anorg. allg. Chemie*, **309**, 289 (1961).
4. J. Casabó, J. Ribas and J. Bartroli, *Rev. Chem. Min.*, **13**, 149 (1976).
5. M.P. Coakley, *Appl. Spectrosc.*, **18**, 149 (1964).
6. K.A. Jensen and P.H. Nielsen, *Acta Chem. Scand.*, **18**, 1 (1964).
7. M. Izquierdo, J. Casabó, C. Díaz and J. Ribas, *Polyhedron*, **2**, 529 (1983).
8. J. Casabó, M. Izquierdo, J. Ribas and C. Díaz, *Transition Met. Chem.*, **8**, 110 (1983).
9. J.R. Durig, R. Layton, D.W. Sink and B.R. Mitchell, *Spectrochim. Acta*, **21**, 1367 (1965).
10. P.H. Nielsen and O. Dahl, *Acta Chem. Scand.*, **20**, 1113 (1966).
11. J.C. Evans, *Spectrochim. Acta*, **16**, 428 (1960).
12. G.M. Watkins, *Ph.D. Thesis*, University of Cape Town, 1988.
13. S. Pinchas and I. Laulicht, *Infrared Spectra of Labelled Compounds*, (Academic Press, London, 1971).
14. B. Marchon, L. Bokobza and G. Cote, *Spectrochim. Acta*, **42A**, 537 (1986).
15. C. Engelter, G.E. Jackson, C.L. Knight and D.A. Thornton, *J. Mol. Struct.*, in press.