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THE INFRARED SPECTRA OF IMIDAZOLE COMPLEXES OF FIRST TRANSITION SERIES METAL(II) NITRATES AND PERCHLORATES

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ABSTRACT

The IR spectra (4000—140 cm^{-1}) of the twelve imidazole (Him) complexes $[M(Him)_6](NO_3)_2$ (M = Co, Ni, Zn); $[M(Him)_6](ClO_4)_2$ (M = Mn, Fe, Co, Ni); $[Zn(Him)_5](ClO_4)_2$; $[Cu(Him)_4X_2]$ (X = NO_3, ClO_4); $[Zn(Him)_4(NO_3)_2]$; $[Zn(Him)_4](ClO_4)_2$ and their deuterated analogues are discussed. The ratio between the frequencies of corresponding bands in the deuterated and undeuterated species is used to assign the internal imidazole vibrations. The internal modes of the NO_3^- and ClO_4^- ions are discussed in relation to the known or proposed structures of the complexes. The metal—ligand vibrations are assigned on the grounds of the shifts which occur on imidazole deuteration and metal ion substitution.

INTRODUCTION

Although the IR spectra of imidazole complexes have been widely studied [1—10] most of the work refers to the halide complexes. No isotopic labelling studies of the metal nitrate and perchlorate complexes have been made. In previous papers [11—13], ν^D/ν^H ratios have been successfully applied to distinguishing between the C—H(D) and ring modes in heterocyclic and aromatic molecules and their metal complexes.

ν^D/ν^H is defined as the ratio between the frequencies of corresponding bands in the IR spectra of a ring-deuterated molecule and its normal (unlabelled) analogue. As described in the preceding paper [13], the ν^D/ν^H values have assisted in resolving the vexed question of assignments in the IR spectrum of imidazole (Him). In this paper we discuss the application of deuteration to the IR spectra of the imidazole complexes $[M(Him)_6](NO_3)_2$ (M = Co, Ni, Zn), $[M(Him)_6](ClO_4)_2$ (M = Mn, Fe, Co, Ni), $[Zn(Him)_5](ClO_4)_2$, $[Cu(Him)_4X_2]$ (X = NO_3, ClO_4), $[Zn(Him)_4(NO_3)_2]$ and $[Zn(Him)_4](ClO_4)_2$.

EXPERIMENTAL

The complexes $[M(Him)_6](NO_3)_2$ (M = Co, Ni) were prepared by slow addition of imidazole (0.003 mole) in water (2 ml) to a solution of the (hydrated) metal(II) nitrate (0.0005 mole) in water (2 ml). The precipitates were collected by filtration and washed with cold water. $[Zn(Him)_6](NO_3)_2$ was isolated from a concentrated ethanol solution of zinc(II) nitrate (0.0005 mole) and imidazole (0.003 mole) which was allowed to stand for two days at room temperature. The crystals were washed with cold ethanol. The complexes $[M(Him)_6](ClO_4)_2$ (M = Mn, Fe, Co, Ni) and $[Zn(Him)_5](ClO_4)_2$ were similarly obtained from aqueous solutions of imidazole (0.003 mole) and the metal(II) perchlorate (0.0005 mole). The Fe(II) complex was prepared under nitrogen. The complexes $[Cu(Him)_4X_2]$ ($X = NO_3$, ClO_4) were readily precipitated when imidazole (0.002 mole) in ethanol (3 ml) was added to the Cu(II) salt (0.0005 mole) in ethanol (3 ml). The complexes $[Zn(Him)_4(NO_3)_2]$ and $[Zn(Him)_4](ClO_4)_2$, being more soluble, were crystallized by slow evaporation of concentrated solutions of imidazole (0.002 mole) and the Zn(II) salt (0.0005 mole) in ethanol (6 ml). The tetrakis (imidazole) complexes were washed with cold ethanol. Purity and composition of all compounds were established by microanalysis (C,H,N).

The Him-d_3 labelled complexes were prepared as described for the unlabelled compounds, employing 1,2,4,5-tetradeuteroimidazole (Him-d_4) of 98% isotopic purity supplied by Merck, Sharp and Dohme (Canada) Ltd. The deuteroimine (ND) groups of Him-d_4 undergo rapid exchange in aqueous or ethanol solution to yield complexes comprising 2,4,5-trideuteroimidazole (Him-d_3). The complexes $[M(Him\text{-}d_4)_6](NO_3)_2$ (M = Co, Ni) were obtained as described for $[M(Him\text{-}d_3)_6](NO_3)_2$ by substitution of D_2O for H_2O. The complex $[Co(Him\text{-}d_1)_6](NO_3)_2$ was similarly obtained from 1-deuteroimidazole (Him-d_1) synthesized by successive recrystallisation of Him-d_4 from D_2O in an atmosphere of nitrogen.

Inrared spectra were determined on Nujol or hexachlorobutadiene mulls between caesium iodide plates (4000—300 cm^{-1}) or polyethylene plates (300—150 cm^{-1}) on Beckman IR-12 and Perkin-Elmer 180 spectrophotometers.

RESULTS AND DISCUSSION

The internal ligand modes of Him were assigned by d_1-, d_3- and d_4-labelling of imidazole in the complex $[Co(Him)_6](NO_3)_2$ and by d_3- and d_4-labelling of $[Ni(Him)_6](NO_3)_2$. The ratios ν^{D_1}/ν^{H_4}, ν^{D_3}/ν^{H_4} and ν^{D_4}/ν^{H_4} were determined and used in relation to the study of the IR spectra of deuterated imidazoles [13] to assign the ligand vibrations. These assignments for the free ligand are applicable to the complexes also, since, apart from some shifts and minor splittings, the ligand spectrum is faithfully reproduced in the spectra of the complexes. The value of the ν^D/ν^H ratio which serves to distinguish between νC—H (or νN—H) and ring modes is 0.83, ratios above this value indicating a ring mode and values below 0.83 indicating νC—H (or νN—H) modes [13].

The complexes $[M(Him)_6](NO_3)_2$ (M = Co, Ni, Zn)

The Co(II) and Ni(II) complexes are isomorphous, occupying the space group $R\bar{3}$ [14, 15]. Complete assignments for the low frequency vibrational spectra of the Co(II) complex result from a single crystal study [10] (for which the complex is suited since the point group, site group and factor group are S_6). The frequencies and shifts are recorded in Table 1. It is clear from the band-for-band correspondence between the spectra that the Zn(II) complex is isostructural with those of Co(II) and Ni(II).

Structural determination of the Ni(II) complex [14] reveals ionic nitrate groups with essentially C_3 symmetry insufficiently distorted from the D_{3h} symmetry of an isolated nitrate ion to cause splitting of degeneracies or to induce activity of IR-inactive modes. Of the four normal vibrational modes of a nitrate ion, ν_1 (which occurs near 1050 cm^{-1}) is IR-inactive but frequently appears in the spectra of complexes in which NO_3^- lies outside the coordination sphere as a result of relaxation of the free ion selection rules under the constraint of the crystal field. The ν_1 band is absent from all three spectra discussed here, while ν_2, ν_3 and ν_4 appear where expected for an ionic nitrate. That the ν_2 band shifts and shows an apparent increase in intensity in the d_3- and d_4-labelled complexes is due to its coincidence with the δC—D mode of coordinated Him-d_3 and Him-d_4.

All the metal-ligand modes are below 300 cm^{-1} (one asymmetric stretch and one N—M—N bend are expected in O_h point group symmetry). It is generally agreed [3, 8—10] that the band of highest frequency is νM—N. The equivalent band in the spectrum of $[M(Him)_6]Cl_2$ (M = Ni, Zn) exhibits the largest metal isotope shifts in this region [8]. Furthermore, the d_3-induced shifts in these bands are of the magnitude expected for a vibrationally pure νM—N band and they are strongly metal ion dependent in the c.f.s.e. sequence Co < Ni > Zn. Four opinions exist as to the origins of the remaining one (or two) bands within the range 140—300 cm^{-1}. One view [9] is that these weaker bands may be components of the T_{1u} stretch arising from departure from O_h symmetry. Eilbeck and co-workers [3] assigned the 200 cm^{-1} band in $[Co(Him)_6]Cl_2$ to δN—Co—N while others [8] consider them to be ligand modes originating in the very weak 180 cm^{-1} band of free Him. However, the 180 cm^{-1} band has elsewhere [16] been assigned to a translational lattice mode. Adams and Trumble [10] have provided the most complete assignment study and suggest that these bands originate in M—Him torsional modes and the bending vibrations δM—N—C. The latter seems the most appropriate assignment and receives support from our labelling study in that the d_3-induced shifts of these bands are frequently higher than those expected [17] and generally observed for νM—N. The δM—N—C mode involves one of the deuterated carbon atoms in the d_3-labelled complex and the mass effect on δM—N—C would be greater than on νM—N which is relatively isolated from the site of deuteration.

TABLE 1

Frequencies (cm^{-1}), ratios ν^D/ν^H and band assignments in the IR spectra of $[M(Him)_6](NO_3)_2$ (M = Co, Ni, Zn)

$[Co(Him)_6](NO_3)_2$				$[Ni(Him)_6](NO_3)_2$			$[Zn(Him)_6](NO_3)_2$		Mean[a]			Assignment
Him	-d_1	-d_3	-d_4	Him	-d_3	-d_4	Him	-d_3	ν^{D_1}/ν^{H_4}	ν^{D_3}/ν^{H_4}	ν^{D_4}/ν^{H_4}	
3185	2403 2389	3185	2393 2375	3173	3173	2398 2380	3100	3100	0.75	1.00	0.75	νN–H
3135	3135	2374		3135	2378		3134	2384	1.00	0.76	0.74	νC–H
3135	3135	2352	2331	3135	2353	2337	3134	2350	1.00	0.75	0.74	νC–H
3135	3135	2332		3135	2336		3134	2340	1.00	0.75	0.74	νC–H
1536	1536	1489 1473	1485 1474	1540	1489 1474	1483 1477	1537	1490	1.00	0.96	0.96	ν ring
1505 1490	1505 1488	1445	1447	1503 1490	1447	1449	1505sh 1490	1448	1.00	0.96	0.97	ν ring
1455sh	1455sh	1455sh	1455sh	1460sh	1460sh	1460sh						
1436	1436	1340sh	1348sh	1439	1359sh	1359sh	1439	1350	1.00	0.94	0.93	ν ring
			1431			1431						
1374	1374	1373	1373	1373	1373	1373	1374	1374				ν_3 NO_3
1323	1323	1285 1268	1283 1265	1326	1290 1273	1290 1271	1324	1290 1270	1.00	0.96	0.96	ν ring
1252	1252 1243	941	941	1255	944	944	1247	941	1.00	0.75	0.75	δC–H
1232	918 905	1187 1178	914	1235	1191 1182	918	1234	1195 1178	0.74	0.96	0.74	δN–H
1179 1170	1180 1171	1155	1187 1167 1155	1183 1174	1160	1191 1173 1161	1180 1172	1158				Comb.
1136	1144 1136	1112	1112	1141	1117	1119	1138	1112	1.00	0.98	0.98	ν ring
1101 1095	1112 1095	890 874	886 873	1104 1099	894 877	891 877	1102 1096	890[b] 874	1.00	0.80	0.80	δC–H
1072 1067sh	1072 1067sh	818	814	1072	821	818	1073 1069sh	817	1.00	0.76	0.76	δCH

970w			996w	977w		1001w						Comb.
939[c]	570 558	899	561sh	938[c]	901	566sh	935[c]	890[b]	0.60	0.95	0.60	γN–H
939[c]	962	969sh 963	969sh 958	938[c]	973 965	975 962	935[c]	971 962	1.02	1.03	1.03	δ ring
939[c]	939	723	723	938[c]	726	726	935[c]	726	1.00	0.77	0.77	γC–H
918	876	840	835	921	845	839	920	840	0.95	0.91	0.91	δ ring
871							870					
861							861	862				
844	843	657	657	848	662	663	848	667	1.00	0.78	0.78	γC–H
825	825	818[d]	814[d]	827	821[d]	818[d]	828	817[d]				ν_2 NO_3
773w	771w	771w	771w	770w	770w	770w	770w	770w				
760w	760w	760w	760w	760w	760w	760w	760w	760w				
746	745	590 577	590 576	747	594 581	594 580	749	592 579	1.00	0.78	0.78	γC–H
710	710	710	710	715	715	715	712	712				ν_4 NO_3
666	666	563	561	670	568	566	667	564	1.00	0.85	0.84	γ ring
614	614	521	520	616	524	524	616	520	1.00	0.84	0.85	γ ring
238		235		261	257		200	194				νM–N
201		193		212	205		159	150				δM–N–C
172		164		185	175							δM–N–C

[a] Mean of ratio for three complexes (maximum deviation = 0.01). [b] γN–H and δC–H coincident. [c] γN–H, γC–H and δ ring coincident.
[d] Nitrate vibration in spectra of Him-d_3 and Him-d_4 are coincident with δC–D, hence the apparent low frequency shift in ν_2 NO_3.
Sh, shoulder; w, weak.

TABLE 2

Frequencies (cm^{-1}), ratios ν^{D_3}/ν^{H_4} and band assignments in the IR spectra of [M(Him)$_6$] (ClO$_4$)$_2$ (M = Mn, Fe, Co, Ni) and [Zn(Him)$_5$](ClO$_4$)$_2$

Mn	Fe	Co	Ni		Zn		Mean[a] ν^{D_3}/ν^{H_4}	Assignment
Him	Him	Him	Him	-d_3	Him	-d_3		
3437 3350	3437 3355	3437 3355	3438 3360	3438 3360	3320	3320	1.00	νN—H
3165	3165	3165	3165	2363	3145	2360	0.75	νC—H
3143	3145	3145	3150	2335	3130	2335	0.74	νC—H
1535	1535	1535	1536	1497 1484	1545	1475	0.96	ν ring
1486	1486	1486	1486	1440	1510 1497	1458	0.97	ν ring
1421	1421	1421	1424	1461 1411 1403	1432	1425	1.00	ν ring
1325	1325	1325	1326	1287 1273	1330 1323sh	1275 1260	0.96	ν ring
1255	1255	1255	1257	948 932	1265	947 933	0.74	δC—H
1223	1223	1223	1223	1166 1159	1245	1190	0.95	δN—H
1156	1156	1156	1156	b	1170	b		ν ring
1130sh	1130sh	1130sh	1130sh	1130sh	1130sh	1130sh		ν_3 ClO$_4$
1111	1111	1111	1111	1111	1110	1110		
1084	1084	1084	1085	1085	1087	1087		
c	c	c	c	883 871	c	891 875		δC—D
1049	1049	1049	1054	820	1071	826	0.77	δC—H
975	975	975	975	972	980			Comb.
936	936	936	936	961	953	973	1.03	δ ring
919	919	919	919	725	920	733sh	0.79	γC—H
876 864	876 864	876 864	876 864					Comb.
845	845	845	845	771	847	778	0.91	δ ring
826	826	826	826	648	833 824	653	0.78	γC—H
770 758	770 758	770 758	771 758	593 579	767 757	577	0.76	γC—H
727	727	727	725	715	725	725	1.00	γN—H
656	656	656	660	567 557	670 650	547	0.84	γ ring
621	621	621	621	621	621	621		ν_4 ClO$_4$
607 595	607 595	607 595	607 595	531 520	609sh	525	0.86	γ ring
464w	464w	464w	464w	464w	464vw	464vw		ν_2 ClO$_4$
211(3)[d]	231(5)[d]	243(4)[d] 224(4)[d]	260	256	322 310 257	310 303 248		νM—N νM—N νM—N

TABLE 2 (continued)

Mn	Fe	Co	Ni		Zn		Mean[a] ν^{D_3}/ν^{H_4}	Assignment
Him	Him	Him	Him	-d_3	Him	-d_3		
278(7)[d]	275(3)[d]	185(3)[d]	199	193	195	184		δM—N—C
168(8)[d]	264(10)[d]	175(6)[d]	185	174				δM—N—C
					176	176		δN—M—N

[a] Mean of ratio for Ni(II) and Zn(II) complexes (maximum deviation = 0.01). [b] Band in spectrum of labelled complex is obscured by perchlorate absorption in 1100 cm^{-1} region. [c] Band in spectrum of unlabelled complex is obscured by perchlorate absorption in 1100 cm^{-1} region. [d] Figures in parentheses following metal—ligand frequencies are the shifts towards lower frequency induced by Him-d_3 labelling. Sh, shoulder; w, weak; vw, very weak.

The complexes [M(Him)$_6$](ClO$_4$)$_2$ (M = Mn, Fe, Co, Ni) and [Zn(Him)$_5$](ClO$_4$)$_2$

Except for splitting of the νCo—N bands in the spectrum of the Co(II) complex, the striking similarity of the band patterns of the complexes of Mn(II) through Ni(II) is sufficient evidence of their isostructural character. The Zn(II) complex is five-coordinate and probably has square-based pyramidal configuration. The mid-IR spectra (Table 2) are characterized by two νN—H bands near 3360 cm^{-1} except for the Zn(II) complex which has a single broad band at 3320 cm^{-1}. Differences also occur with respect to the γ ring mode near 600 cm^{-1} which exhibits two bands in the complexes of Mn(II) through Ni(II) but which appears as a shoulder at 609 cm^{-1} in the Zn(II) spectrum. Only the Co(II) complex has previously received any attention [9]. Its magnetic moment (μ_{eff} = 5.10 B.M.) and electronic spectrum are typical of spin-free octahedral Co(II). It was concluded [9] from the mid-IR spectrum that the perchlorate groups are ionic.

The nine vibrational degrees of freedom of the T_d point group free perchlorate ion are distributed over the four fundamental vibrational modes: $A_1(\nu_1) + E(\nu_2) + 2T_2(\nu_3, \nu_4)$. The triply degenerate modes are IR-active, ν_3 occurring near 1100 cm^{-1} as an (occasionally split) broad band while ν_4 is observed near 625 cm^{-1}. The non-degenerate ν_1 band, theoretically IR-forbidden, often occurs as a weak band near 930 cm^{-1} because of relaxation of the T_d symmetry criteria in a field of lower symmetry [18, 19]. Coordination of the perchlorate group induces marked differences from the free ion spectrum as a result of lowering of symmetry and vibrational coupling. The perchlorate bands of the complexes under discussion conform with those expected for the free ion except insofar as activation of the ν_2 mode produces very weak bands near 460 cm^{-1}. Possible activation of ν_1 cannot be ruled out due to masking by imidazole bands in the 930 cm^{-1} region. The ν_2, ν_3 and ν_4 perchlorate assignments are confirmed by absence of sensitivity to imidazole deuteration.

TABLE 3

Frequencies (cm^{-1}), ratios ν^{D_3}/ν^{H_4} and band assignments in the IR spectra of [Cu(Him)$_4$(ClO$_4$)$_2$] and [Zn(Him)$_4$](ClO$_4$)$_2$

Cu(II)		Zn(II)		Mean^{a} ν^{D_3}/ν^{H_4}	Assignment
Him	-d_3	Him	-d_3		
3381 3351	3381 3351	3380	3380	1.00	νN—H
3164	2372	3160	2379	0.75	νC—H
3144	2340	3145	2355	0.75	νC—H
		3131	2337	0.75	νC—H
1545	1486 1471	1546	1493	0.96	ν ring
1513 1493	1465 1454	1512 1508sh	1471 1453	0.97	ν ring
1434	1421 1409	1431	1404	0.98	ν ring
			1347 1339		
1330	1303 1276	1331	1273	0.96	ν ring
1266	950	1267	948	0.75	δC—H
1225	1198 1183	1230	1188		Comb.
1175	b	1183	b		ν ring
c	c	1133	c		δN—H
1135sh 1111 1070	1135sh 1111 1070	1120—1060^{d}			ν_3 ClO$_4$
e	890 877^{f}	e	889		δC—D
1056	827	1050	828	0.78	δC—H
950	980 970	953	974	1.02	δ ring
930w	930w				ν_1 ClO$_4$
917	745 738^{f}	920	930 759 741	0.81	γC—H
870	845	873			
847	781 776	854 847	776	0.92	δ ring
g	650 644	833	g		γC—H
764 757	598 586^{f}	760	600	0.78	γC—H
	760				
721	715	730	720	0.99	γN—H
660 650	565 552	652	556	0.85	γ ring
625	625	622	622		ν_4 ClO$_4$
610	521	614	524	0.85	γ ring

TABLE 3 (continued)

Cu(II)		Zn(II)		Mean[a] ν^{D_3}/ν^{H_4}	Assignment
Him	-d_3	Him	-d_3		
462vw	462vw	464vw	464vw		ν_2 ClO_4
307	303				νCu—N asym.
286	284				νCu—N sym.
		271	268		νZn—N
240	238	199	189		δM—N—C
228	219	185	175		δM—N—C
167	162				δN—Cu—N

[a] Mean of ratios for Cu(II) and Zn(II) complexes. [b] Band in spectrum of labelled complex obscured by perchlorate absorption near 1100 cm^{-1}. [c] Band obscured by perchlorate absorption near 1100 cm^{-1}. [d] Perchlorate band in spectrum of the Zn(II) complex occurs as a continuous absorption in the range 1120—1060 cm^{-1}. [e] Band in spectrum of unlabelled complex obscured by perchlorate absorption near 1100 cm^{-1}. [f] Mean of doublet. [g] Band not observed. Sh, shoulder; w, weak; vw, very weak.

The far-IR spectra receive the same assignments that were provided for the nitrate complexes. Splitting of νCo—N suggests that the Co(II) complex may deviate from the regular octahedral structure implied by its magnetic moment [9]. Both components of the νCo—N band are equally shifted ($\Delta\nu$ = 4 cm^{-1}) by imidazole deuteration. The c.f.s.e. sequence Mn < Fe < Co < Ni is followed by νM—N.

Apart from the differences in the mid-IR region mentioned above, the five-coordinate Zn(II) complex has relatively high values of νZn—N as expected from the lower coordination number. Furthermore, the far-IR region comprises five bands below 400 cm^{-1} as opposed to three or four for the octahedral complexes. It would seem reasonable to assign the three bands in the region 250—350 cm^{-1} to the three IR-active νZn—N modes expected for a $[Zn(Him)_5]^{2+}$ cation with C_{4v} symmetry (tetragonal bipyramidal structure).

The complexes $[Cu(Him)_4(ClO_4)_2]$, $[Zn(Him)_4](ClO_4)_2$ and $[M(Him)_4](NO_3)_2$ (M = Cu, Zn)

The perchlorate groups of $[Cu(Him)_4(ClO_4)_2]$ may be considered just within the coordination sphere (Cu—O distance 2.625 Å) yielding an essentially six-coordinate tetragonal complex with four co-planar coordinate nitrogen atoms [20]. The hydrogen atoms on the imidazole nitrogens form hydrogen bonds with the perchlorate oxygen atoms as suggested by the IR spectrum (Table 3) which reveals doubling of νN—H. The crystal structure shows that the monodentate perchlorates approximate the symmetry of the free ion. Tetragonal distortion along the Cu—O bonds evidently lowers the Cu—O covalent character. This is apparent from the IR spectrum where the

TABLE 4

Frequencies (cm^{-1}), ratios ν^{D_3}/ν^{H_4} and band assignments in the IR spectra of [Cu(Him)$_4$(NO$_3$)$_2$] and [Zn(Him)$_4$(NO$_3$)$_2$]

Cu(II)		Zn(II)		Mean^{a} ν^{D_3}/ν^{H_4}	Assignment
Him	-d_3	Him	-d_3		
3315	3310	3237	3237	1.00	νN—H
	2356	3160^{b}	2363	0.75	νC—H
3155	2343	3148	2355	0.75	νC—H
3134	2329	3136^{b}	2334^{b}	0.74	νC—H
1537	1484 1472	1544	1498	0.96	ν ring
1498	1450	1512 1505	1478 1466 1433	0.97	ν ring
1432	1404sh	1461	1431	0.98	ν ring
1399	1390	1406	1394		ν_4 NO$_3$
1343	1337	1324	1335		ν_1 NO$_3$
1322 1311sh	1292 1272	1315	1289 1270	0.97	ν ring
1257	946 937	1261	945 940	0.75	δC—H
1242	1190	1248	1210		
	1174	1238	1196		
	1166				
	1147				
1167	1110	1189	1117	0.94	ν ring
1132	1080	1136	1079	0.95	δN—H
1097	888^{b} 876	1104 1092	891	0.80	δC—H
1068	819	1069	831 819	0.77	δC—H
1044	1049	1035	1035		ν_2 NO$_3$
			1010		
949 942	975 968	954	971	1.03	δ ring
931 925	757 736	919 912	736	0.80	γC—H
890		865			
856 846	773	842sh 835	770	0.91	δ ring
823	823sh	813	813sh		ν_6 NO$_3$
761 746	595^{b} 580^{b}	768 760	597 593	0.78	γC—H
739sh	722	745	^{c}	0.98	γN—H
		718	718		ν_3 NO$_3$
709	709	703	703		ν_5 NO$_3$
660	567 560	644	551 549	0.85	γ ring
619	529	623	530sh	0.85	γ ring
610	519	618	524		

TABLE 4 (continued)

Cu(II)		Zn(II)		Mean[a] ν^{D_3}/ν^{H_4}	Assignment
Him	$-d_3$	Him	$-d_3$		
290	287	271	267		νM—N
254	246				δM—N—C
223	216	202	194		δM—N—C
165	157	156	154		δN—M—N

[a] Mean of ratios for Cu(II) and Zn(II) complexes. [b] Mean of doublet. [c] Band in spectrum of labelled complex not observed (possibly coincident with 736 cm^{-1} band). Sh, shoulder.

ν_3 perchlorate band displays structure characteristic of the ionic perchlorates in $[M(Him)_6](ClO_4)_2$. The asymmetric deformation, ν_4, occurs as a single band at 625 cm^{-1} while IR-forbidden ν_1 and ν_2 appear weakly at 930 and 462 cm^{-1}. All of these assignments receive support from absence of sensitivity to imidazole deuteration.

Crystal structure determination of $[Zn(Him)_4](ClO_4)_2$ reveals tetrahedral Zn(II) [21]. The perchlorate spectrum is similar to that of the ionic perchlorates in the hexakis(imidazole) complexes except that ν_3 displays no structure. Unlike $[Cu(Him)_4](ClO_4)_2]$, ν_1 is absent from the spectrum of the Zn(II) complex.

In C_i site symmetry, two νCu—N bands are expected for $[Cu(Him)_4(ClO_4)_2]$ and two are observed by contrast with the tetrahedral $[Zn(Him)_4](ClO_4)_2$ (T_d site symmetry) for which one νZn—N band is expected and observed.

$[Cu(Him)_4(NO_3)_2]$ structurally resembles the analogous perchlorate (Cu—O distance 2.57Å) [22]. That the nitrato groups are essentially coordinated to the Cu(II) ion is apparent from the nitrate IR bands (Table 4) which differ from those of the complexes $[M(Him)_6](NO_3)_2$. In the Cu(II) complex the nitrate group symmetry is lowered from D_{3h} to approximate C_{2v} symmetry, thus lifting degenerate modes and activating all six vibrational degrees of freedom [23, 24]. It is apparent from Table 4 that the nitrate group absorptions of $[Zn(Him)_4(NO_3)_2]$ are similar to those of the Cu(II) complex (except for the absence of ν_3 from the spectrum of the latter, where it is probably unresolved from ν_5) and that both molecules therefore contain monodentate nitrato groups. The position of νN—O in monodentate nitrato complexes is symptomatic of the strength of the M—O covalency [24]. Comparison of the frequencies in Table 4 for the Cu(II) and Zn(II) complexes shows that ν_2 (νN—O) for monodentate nitrate in the Zn(II) complex is 14 cm^{-1} lower in frequency than the corresponding band in the Cu(II) complex, indicating higher covalency in the Zn—O bands. This is consistent with the observed distortion [22] of the Cu(II) complex involving elongation of the axial Cu—O bonds.

The M—N stretches in the spectra of $[M(Him)_4(NO_3)_2]$ (M = Cu, Zn) occur as single bands at 290 and 271 cm^{-1}, respectively. It has been suggested

[4] that the 271 cm^{-1} band in the Zn(II) complex is νZn—O. This seems unlikely for two reasons. Firstly, it has a *d*-sensitivity matching that of most bands assigned to νM—N in the complexes studied here and secondly, it is unlikely that νZn—O would occur some 69 cm^{-1} higher than any other band which may reasonably be assigned to νZn—N (i.e. the band at 199 cm^{-1}). The assignment proposed here yields the expected c.f.s.e. sequence of νM—N: Cu > Zn.

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REFERENCES

1 J. R. Ferraro, Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, 1971, p. 202.
2 D. G. Holah and J. P. Fackler, Inorg. Chem., 4 (1965) 1112.
3 W. J. Eilbeck, F. Holmes, C. E. Taylor and A. E. Underhill, J. Chem. Soc. A, (1968) 128, 1189.
4 D. M. L. Goodgame, M. Goodgame, P. J. Hayward and G. W. Rayner Canham, Inorg. Chem., 7 (1968) 2447.
5 C. Perchard and A. Novak, J. Chim. Phys., 65 (1968) 1964.
6 C. E. Taylor and A. E. Underhill, J. Chem. Soc. A, (1969) 368.
7 C. Perchard and A. Novak, Spectrochim. Acta, Part A, 26 (1970) 871.
8 B. C. Cornilsen and K. Nakamoto, J. Inorg. Nucl. Chem., 26 (1974) 2467.
9 W. J. Davis and J. Smith, J. Chem. Soc. A, (1971) 317.
10 D. M. Adams and W. R. Trumble, J. Chem. Soc. Dalton Trans., (1975) 30.
11 A. T. Hutton and D. A. Thornton, Spectrochim. Acta, Part A, 34 (1978) 645.
12 G. A. Foulds, J. B. Hodgson, A. T. Hutton, M. L. Niven, G. C. Percy, P. E. Rutherford and D. A. Thornton, Spectrosc. Lett., 12 (1979) 25.
13 J. B. Hodgson, G. C. Percy and D. A. Thornton, J. Mol. Struct., 66 (1980) 75.
14 A. Santoro, A. D. Mighell, M. Zocchi and C. W. Reimann, Acta Crystallogr., Sect. B, 25 (1969) 842.
15 M. Gerloch and P. N. Quested, J. Chem. Soc. A, (1971) 3729.
16 C. Perchard and A. Novak, J. Chem. Phys., 48 (1968) 3079.
17 S. Pinchas and I. Laulicht, Infrared Spectra of Labelled Compounds, Academic Press, New York, 1971, p. 38.
18 S. D. Ross, Spectrochim. Acta, 18 (1962) 225.
19 B. J. Hathaway and A. E. Underhill, J. Chem. Soc., (1961) 3091.
20 G. Ivarsson, Acta Chem. Scand., 27 (1973) 3523.
21 C. A. Bear, K. A. Duggan and H. C. Freeman, Acta Crystallogr., Sect. B, 31 (1975) 2713.
22 D. L. McFadden, A. T. McPhail, P. M. Gross, C. D. Garner and F. E. Mabbs, J. Chem. Soc. Dalton Trans., (1976) 47.
23 J. R. Ferraro, Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, 1971, p. 77.
24 B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, J. Chem. Soc., (1957) 4222.