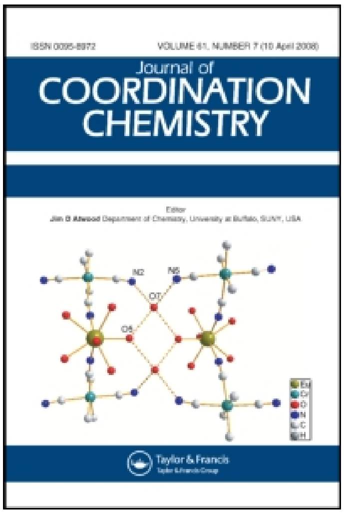

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The Infrared Spectra (4000-50 cm^{-1}) of Complexes of 2,2'-Bipyridine, 1,10-Phenanthroline and their Perdeuterated Analogues with Metal(II) Perchlorates of the First Transition Series

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THE INFRARED SPECTRA (4000–50 cm^{-1}) OF COMPLEXES OF 2,2′-BIPYRIDINE, 1,10-PHENANTHROLINE AND THEIR PERDEUTERATED ANALOGUES WITH METAL(II) PERCHLORATES OF THE FIRST TRANSITION SERIES

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A full infrared assignment (4000 to 50 cm^{-1}) for [M(bipy)$_3$](ClO$_4$)$_2$ and [M(phen)$_3$](ClO$_4$)$_2$ (M = Mn, Fe, Co, Ni, Cu, Zn; bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline) and their fully deuterated analogues is presented. Several ligand bands show metal sensitivity in both series of complexes, but less so with phen. In the Jahn–Teller distorted [Cu(phen)$_3$](ClO$_4$)$_2$ complex only three ligand bands show splitting, accounting for earlier postulations of the absence of J–T distortion based on spectroscopic evidence. Vibrations previously ascribed to activated ligand bands are identified as M–N bends, as combination bands, or are more fully characterized.

Keywords: Infrared, 2,2′-bipyridine, 1,10-phenanthroline, deuteration, metal(II) perchlorates

INTRODUCTION

The deuteration study of the M(II)(ClO$_4$)$_2$ complexes with *tris*-2,2′-bipyridine (bipy)$_3$, and *tris*-1,10-phenanthroline (phen)$_3$, has been undertaken for several reasons.

First, it was initially thought that a comparison between the spectra of the Cu(II) *tris*-complexes with these two ligands clearly demonstrated restriction of the Jahn–Teller induced tetragonal distortion in a Cu(II) complex by the limited capacity of a ligand for expanding its bite (N–N distance). In noting the splitting of the 625, 660 cm^{-1} bipy doublet into a triplet, Inskeep[1] was the first to suggest spectroscopic evidence for tetragonal distortion in the [Cu(bipy)$_3$]$^{2+}$ cation. He also suggested that the absence of splitting in the infrared spectrum of the [Cu(phen)$_3$]$^{2+}$ cation indicated the absence of tetragonal distortion as a result of the more rigid ligand. Percy and Thornton[2–4] extended the infrared investigation of these complexes to 200 cm^{-1}, and from the splitting of the M–N stretching frequencies in [Cu(bipy)$_3$](ClO$_4$)$_2$ and its apparent absence in [Cu(phen)$_3$](ClO$_4$)$_2$, concurred with Inskeep. Unfortunately, these studies were at the extreme end of the range for the instrumentation used, and therefore subject to poor resolution. Two far-infrared metal isotope labelling studies (to 150 and 100 cm^{-1} respectively) of these complexes

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made by Nakamoto and his co-workers[5,6] later revealed both more vibrational bands and a greater splitting by the Cu(II) complexes in the metal–nitrogen stretching and bending region than had previously been reported. Finally, publication of the crystal structures of both $[Cu(bipy)_3](ClO_4)_2$ and $[Cu(phen)_3](ClO_4)_2$[7,8] conclusively shows that *both* tris-bidentate complexes are tetragonal as a result of a static Jahn–Teller distortion. Therefore a full assignment of the $[M(phen)_3](ClO_4)_2$ complexes is necessary to investigate whether spectroscopic evidence for the tetragonal distortion of the Cu(II) was previously overlooked or, alternatively, to determine why it was considered to be absent.

Secondly, the far-infrared assignments (below 200 cm^{-1}) reported for these complexes did not take into account the metal–ligand bending modes. In the complexes of both ligands, several bands were generally described by Nakamoto and his co-workers as being activated ligand bands.[5,6,9] A full vibrational assignment should therefore be useful in distinguishing between internal ligand modes and the metal–nitrogen vibrations.

Thirdly, although several deuteration studies of M(II) complexes with bipy have been made,[10–12] no systematic ligand isotope labelling study has been attempted for the metal(II) complexes of the first transition metal series, nor has there been a ligand isotope study reported for any metal complex with phen.

EXPERIMENTAL

The infrared spectra were recorded on a Perkin Elmer 983 spectrophotometer using both Nujol mulls (2000 to 200 cm^{-1}) and hexachlorobutadiene mulls (4000 to 2000 and 1500 to 1200 cm^{-1}) between CsI plates. Far-infrared spectra were recorded in Nujol mulls (500 to 50 cm^{-1}) between polyethylene plates on a Digilab FTS 16 B/D interferometer. 2,2'-Bipyridine-d_8 (98% isotopic purity) and 1,10-phenanthroline-d_8 (98% isotopic purity) were supplied by Merck, Sharp and Dohme (Canada) Ltd. All Fe(II) complexes were prepared under nitrogen, using nitrogen-purged solvents.

$[M(bipy)_3](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn)

A 5 cm^3 hot aqueous solution of 0.1 g (0.27 mmol) of metal perchlorate (as the hydrated salt) was added to a hot solution of 0.17 g (1.10 mmol; 4 : 1 mol ratio) of 2,2'-bipyridine in 10 cm^3 of 96% EtOH, with stirring. The solution was allowed to cool and the precipitate filtered and washed with absolute EtOH. The complex was recrystallized from the minimum amount of hot acetone and dried over silica gel, under reduced pressure. Yields of 86 to 98% were obtained. Microanalytical data are given in Table I.

The deuterated complexes were prepared as for their -d_0 analogues, at one-half the previous scale. Yields of 80 to 94% were obtained. Microanalytical data are given in Table I.

$[M(phen)_3](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn)

A solution of 0.1 g (0.27 mmol) of metal perchlorate (as the hydrated salt) in 3 cm^3 96% EtOH was added to a solution of 0.16 g (0.82 mmol; 3:1 mol ratio) of 1,10-phenanthroline monohydrate in 7 cm^3 of 96% EtOH, with stirring. The resulting precipitate was filtered and washed with small amounts of water and ethanol. The complex was recrystallized from the minimum amount of hot acetone and dried over silica gel under reduced pressure. Yields of 64 to 98% were obtained. Microanalytical data are given in Table I.

The deuterated complexes were prepared as for their -d_0 analogues, at one-half the previous scale. Yields of 73 to 98% were obtained. Microanalytical data are given in Table I.

TABLE I
Microanalyses of $M(II)(ClO_4)_2$ complexes.

		Experimental			Calculated		
	Colour	%C	%H	%N	%C	%H	%N
$[Mn(bipy)_3](ClO_4)_2$	lemon yellow	49.60	3.45	11.70	49.88	3.35	11.63
$[Fe(bipy)_3](ClO_4)_2{\cdot}1\frac{1}{2}H_2O$	crimson	48.10	3.45	10.95	48.02	3.65	11.20
$[Co(bipy)_3](ClO_4)_2$	sand-yellow	49.65	3.35	11.65	49.60	3.33	11.57
$[Ni(bipy)_3](ClO_4)_2$	pink	49.70	3.40	11.55	49.62	3.33	11.57
$[Cu(bipy)_3](ClO_4)_2$	royal blue	49.10	3.30	11.50	49.29	3.31	11.50
$[Zn(bipy)_3](ClO_4)_2$	white	49.10	3.30	11.45	49.17	3.30	11.47
$[Mn(bipy\text{-}d_8)_3](ClO_4)_2$	lemon yellow	48.10	3.30	11.20	48.26	3.24	11.26
$[Fe(bipy\text{-}d_8)_3](ClO_4)_2{\cdot}\frac{1}{2}H_2O$	crimson	47.65	3.45	11.00	47.63	3.33	11.11
$[Co(bipy\text{-}d_8)_3](ClO_4)_2$	sand-yellow	47.90	3.25	11.25	48.01	3.22	11.20
$[Ni(bipy\text{-}d_8)_3](ClO_4)_2$	pink	47.55	3.25	11.20	48.02	3.22	11.20
$[Cu(bipy\text{-}d_8)_3](ClO_4)_2$	royal blue	47.60	3.25	11.20	47.71	3.20	11.13
$[Zn(bipy\text{-}d_8)_3](ClO_4)_2$	white	47.45	3.30	11.10	47.60	3.20	11.10
$[Mn(phen)_3](ClO_4)_2{\cdot}H_2O$	mustard	53.25	3.35	10.40	53.21	3.22	10.34
$[Fe(phen)_3](ClO_4)_2{\cdot}3\frac{1}{2}H_2O$	post box red	50.15	3.55	9.70	50.37	3.64	9.79
$[Co(phen)_3](ClO_4)_2{\cdot}H_2O$	dark yellow	53.00	3.20	10.30	52.96	3.21	10.29
$[Ni(phen)_3](ClO_4)_2{\cdot}H_2O$	flesh pink	53.20	3.20	10.30	52.97	3.21	10.30
$[Cu(phen)_3](ClO_4)_2{\cdot}\frac{1}{2}H_2O$	dark egg blue	53.25	3.10	10.30	53.24	3.10	10.35
$[Zn(phen)_3](ClO_4)_2{\cdot}H_2O$	white	52.70	3.20	10.25	52.54	3.18	10.21
$[Mn(phen\text{-}d_8)_3](ClO_4)_2{\cdot}H_2O$	mustard	52.00	3.20	10.00	51.68	3.13	10.04
$[Fe(phen\text{-}d_8)_3](ClO_4)_2{\cdot}3H_2O$	post box red	49.85	3.45	9.50	49.50	3.46	9.62
$[Co(phen\text{-}d_8)_3](ClO_4)_2{\cdot}H_2O$	dark yellow	51.60	3.20	10.00	51.43	3.12	10.00
$[Ni(phen\text{-}d_8)_3](ClO_4)_2{\cdot}H_2O$	flesh pink	51.60	3.15	9.95	51.45	3.12	10.00
$[Cu(phen\text{-}d_8)_3](ClO_4)_2{\cdot}H_2O$	duck egg blue	51.40	3.10	9.85	51.15	3.10	9.94
$[Zn(phen\text{-}d_8)_3](ClO_4)_2{\cdot}H_2O$	white	51.30	3.00	10.00	51.04	3.09	9.92

RESULTS AND DISCUSSION

Full infrared assignments of the M(II) complexes of bipy, phen and their perdeuterated analogues are based upon the assignments of the free ligands[13–16] and are shown in Tables II to V. The far-infrared assignments reflecting the deuteration shifts found in this work as well as reported metal–isotope shifts[5,6,9,17] are presented in Tables VI and VII.

TABLE II
Infrared assignment (4000–350 cm^{-1}) of $[M(bipy)_3](ClO_4)_2$ complexes.

Mn	Fe	Co	Ni	Cu	Zn	Assignment
	3533 mbr					νO–H (H_2O)
3196 vw				3135 w	3145 vw	comb
3110 m	3114 m	3110 m	3112 m	3112 m 3102 m	3113 m	2(νC–H)
3079 ms	3086 ms	3077 ms	3081 ms	3089 ms	3082 ms	20b(νC–H)
3069 ms	3078 msh	3069 msh	3065 msh	3071 ms 3067 ms	3070 msh	2′, 7b, 20a and 20b′ (νC–H)
3050 mwsh	3037 vw	3046 mw	3046 mw	3040 msh	3046 m	7b′(νC–H)
3021 mw		3024 mw	3027 mw	3023 w	3024 m	20a(νC–H)
2988 vw	2979 w		2960 vw	2970 vw	2956 vw	comb
2781 w	2780 w	2778 w	2782 w	2783 vw	2782 vw	
2736 w	2738 vw	2738 w	2736 vw	2732 vw	2738 vw	
	2685 vw		2648 vw		2670 vw	
2551 w			2558 vw		2555 vw	
2523 w		2525 vw	2527 vw		2524 vw	
2462 vw	2465 vw	2463 w	2462 vw	2465 vw	2465 vw	
2340 w	2340 vw		2335 vw	2334 w	2340 vw	
2265 w	2266 w	2264 w	2264 w	2265 w	2262 w	
2015 mw	2006 mw	2008 m	2009 mw	2014 wm	2010 w	
1990 wsh	1994 mw	1996 mw	1998 mw			
1951 vw	1950 vw	1955 vw	1955 vw	1951 vw	1958 w	
1921 w		1925 w	1923 w	1936 w	1928 w	
1892 vwsh	1908 w	1915 w	1913 w	1915 vw	1920 w	
1867 vw		1853 w	1850 w	1856 w	1868 w	
1780 wbr		1775 w	1773 w	1780 vw	1780 vwbr	
1720 wbr		1728 w	1731 w	1730 wbr		
		1700 w	1702 w	1709 w	1715 wbr	
1673 vw	1682 vw		1680 vw		1675 w	
1634 vw	1627 wm	1634 vw	1650 vw	1665 wbr	1644 w	
1621 vw		1620 vw	1625 vw			
1602 vs	1607 vs	1607 vs	1607 vs	1607 vs 1597 s	1607 vs	8b′(νring)
1596 s	1600 s	1602 s	1602 vs	1602 vs 1591 s	1598 s	8b(νring)
1575 m	1574 wm	1574 m	1574 m	1575 m	1577 ms	8a′(νring)
1566 wm	1567 m	1564 wm	1564 m	1567 m	1567 m	8a(νring)
1491 ms	1495 m	1496 m	1494 ms	1497 ms 1492 ms	1492 m	19a′(νring)
1475 s	1465 s	1473 s	1471 s	1486 ms 1472 s	1474 s	19a(νring)
1440 vs	1443 vs	1439 vs	1441 vs	1441 vs	1440 vs	19b′(νring)
	1425 ms	1418 m	1419 msh			19b(νring)

TABLE II (*continued*)

Mn	Fe	Co	Ni	Cu	Zn	Assignment
1366 w	1372 m	1372 m	1375 w	1368 w	1368 w	comb
1315 ms	1315 ms	1315 ms	1315 ms	1320 ms 1314 ms	1315 ms	A(νinter-ring)
1281 vw	1281 vw	1285 vw	1281 w	1281 vw	1284 w	3′(αC–H)
1262 vw	1272 w	1265 w	1265 w	1270 w	1266 w	14′(νring)
1246 s	1246 s	1246 s	1246 s	1247 s	1250 s	3(αC–H)
1226 m 1219 m	1222 m	1220 m	1219 m	1218 m	1222 m	14(νring)
1172 s	1168 s	1172 s	1171 s	1173 m 1167 m	1172 s	15′(αC–H)
1157 s	1160 s	1159 m	1158 m	1159 s	1158 s	15(αC–H)
				1105 vssh		9b′(αC–H)
1082 vsbr	1092 vsbr	1088 vsbr	1089 vsbr	1087 vsbr	1085 vsbr	$\nu_a(\mathrm{ClO_4})$ and 9b(γC–H)
	1070 s	1070 s	1072 s			18b(αC–H)
1044 ssh		1045 s	1044 ssh	1047 s	1044 s	18b′(αC–H)
1018 ssh	1024 s	1021 s	1023 s	1027 ms	1021 s	12(νring)
1014 s	1012 ms	1016 s	1017 ssh 1008 ssh	1020 ms 1006 msh	1014 s	1(νring)
1001 s	1000 mw	998 w	1000 wsh	996 ms	1000 ms	12′(νring)
984 w 973 wm				985 ms 971 w	986 w	5(γC–H)
960 w	956 w	964 wm 959 wsh	964 m	967 mw	966 w 962 w	5′(γC–H)
930 vw	930 w	929 w	929 w	930 w	929 w	$\nu_s(\mathrm{ClO_4})$
903 w		896 w	895 w	905 w	899 wm	10b′(γC–H)
891 wsh	879 mw	892 mw	890 mw	891 w	894 wm	10b(γC–H)
	826 w		816 wsh	813 w	819 wsh	10a′(γC–H)
812 w		813 w	813 w	809 w	815 w	10a(γC–H)
772 s	768 s	775 s	775 s	770 s	777 s	4(γring)
760 s	765 s	768 s	768 s	765 s 762 s	767 sbr	1′(νring)
747 s				749 ms		11′(γC–H)
737 s	734 s	736 s	736 s	735 s	737 s	11(γC–H)
723 wsh	727 wsh	723 wsh	725 wsh	722 wsh	720 wsh	4′(γring)
651 ms 646 m	656 m 650 m	653 ms	653 ms	658 m 652 m	653 ms	6b(νring)
		634 m	635 m	634 wsh	632 ms	6a(νring)
623 s	623 s	623 s	623 s	623 s	623 s	$\delta(\mathrm{ClO_4})$ and 6b′(νring)
550 vw	550 vw	550 vw		550 vw		comb
	497 w	481 w	483 w	496 w 481 w	494 vw	comb

TABLE II (*continued*)

Mn	Fe	Co	Ni	Cu	Zn	Assignment
467 w	475 wm	465 vw	468 w	465 vw	478 w	ε(ring scissors)
	456 w	455 vw	458 vw	458 w	459 w	Γ(ring sheer)
424 w	438 wsh	433 m	439 m	441 m 423 m	428 ms	16b(γring)
412 ms	418 ms	413 ms	413 s	410 ms 393 msh	413 s	16a(γring)

s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad, comb = combination.

TABLE III

Infrared assignment (4000–350 cm^{-1}) of [M(bipy-d_8)$_3$](ClO$_4$)$_2$ complexes.

Mn	Fe	Co	Ni	Cu	Zn	Assignment
	3524 wmbr					νO-H (H$_2$O)
	3189 wbr					
			3143 vw	3140 vw	3136 vw	comb
3131 wbr			3130 vw	3130 vw	3128 vw	
2993 vw		2997 vw	2995 vw		2994 vw	
2923 w	2925 w	2925 w	2920 vw	2920 vw	2922 w	
2854 vw	2850 vw	2853 vw	2850 vw	2850 vw	2854 vw	
2780 w	2780 vw	2776 w	2778 w	2778 w	2778 w	
2656 w	2664 w	2656 w	2666 w	2665 w	2660 w	
2583 w		2581 vw	2576 vw		2584 vw	
2505 w	2506 w	2516 w	2519 w		2511 w	
2474 w	2470 vw	2472 vw	2480 vw		2480 vw	
2408 vw	2410 wbr	2410 w	2408 vw	2405 vw	2407 vw	
		2334 wm	2335 w	2334 w		
2308 wm	2312 wm	2310 wm	2312 w	2305 wm	2308 wm	2(νC–D)
2295 m	2298 m		2288 wm	2295 msh	2294 ms	2′, 20b′ and 7b′ (νC–D)
		2282 wmsh				
2275 wsh	2280 msh		2282 wmsh	2291 m	2283 msh	20b and 20a′ (νC–D)
2270 wsh	2263 wsh	2270 m	2273 m	2261 w	2274 msh	20a and 7b (νC–D)
2186 w	2188 w			2182 vw	2188 w	comb
2017 mw	2012 w	2029 w	2032 w	2022 mw	2022 mw	
2003 wsh		2006 wm	2008 wm		2005 msh	
		1996 wm	1998 wm	1998 wmsh	1990 wsh	
1919 w	1920 w	1919 w	1918 w	1918 w	1920 w	
1804 w		1802 w	1804 w	1802 w	1804 w	
	1798 w	1796 mw		1797 wm	1796 w	
1698 vw	1699 w	1700 vw		1694 vw	1700 wsh	
1682 w			1683 w		1683 w	
1645 w	1634 w	1640 vw	1643 vw	1650 w	1650 vw	
1601 w	1608 w	1594 w	1595 w	1598 w	1599 w	
1574 s	1576 s	1576 s	1578 s	1577 ms 1569 ms	1572 s	8b′(νring)

TABLE III (*continued*)

Mn	Fe	Co	Ni	Cu	Zn	Assignment
1560 s	1564 s	1566 s	1566 s	1562 ms	1563 ms	8b(νring)
1543 s	1542 s	1542 s	1546 s	1544 s	1544 s	8a′(νring)
	1538 s					
1530 vs		1530 s	1532 s	1532 s	1530 s	8a(νring)
	1532 s					
1466 w	1466 w	1466 w		1468 w	1463 w	comb
				1433 ms		
1420 ms	1428 ms	1425 ms	1428 ms		1420 ms	19a′(νring)
				1418 ms		
1389 vw	1389 w		1389 vw	1391 vw	1387 vw	comb
1361 vw	1370 w	1367 vw	1361 vw	1361 vw	1366 vw	comb
1344 vw	1342 msh	1342 w	1342 w		1345 w	19b′(νring)
				1333 s		
1330 vs	1334 vs	1334 vs	1334 vs		1331 vs	19a(νring)
				1326 s		
1308 m	1301 m	1306 mw	1308 mw	1303 mw	1307 mw	19b(νring)
1271 vw		1270 vw	1271 vw	1270 vw	1267 w	comb
1257 vw	1259 vw	1261 vw	1262 vw	1262 vw	1256 vw	14(νring)
1237 s	1236 s	1240 s	1240 s	1240 s	1240 s	A(νinter-ring)
1200 w	1201 w	1201 vwbr	1202 vwbr	1206 w	1201 w	comb
1169 vw		1167 vw	1167 vw	1167 vw	1169 vw	14′(νring)
		1108 ssh	1109 ssh			
1095 vsbr	1088 vsbr	1091 vsbr	1095 vsbr	1088 vsbr	1091 vsbr	$\nu_a(ClO_4)$
		1070 ssh				
1031 m				1029 ms	1030 s	
						12(νring)
1023 ms	1023 mssh	1020 m	1021 mw	1021 m	1022 s	
				1009 wm		
1005 wm	1003 s	1003 s	1004 s		1004 s	1(νring)
				1003 wm		
				996 m		
989 s	993 s	993 m	994 ms		992 s	12′(νring)
				992 ms		
978 s	980 s	983 s	985 s	978 m	983 s	3(αC–D)
964 wm	966 mw	964 mw		970 m	970 m	3′(αC–D)
931 w	929 wm	929 w	930 w	931 w	929 w	$\nu_s(ClO_4)$
877 vw			875 vw	879 vw		comb
		868 s	868 ms	865 m	870 s	9b′(αC–D)
866 s						
	867 s	860 s	862 ms	855 msh	861 s	
						9b(αC–D)
853 s				851 ms		
843 mw		840 ms	843 msh	840 ms	839 m	15′(αC–D)
	829 ms	836 m	839 ms			15(αC–D)
832 s	820 ms	832 ms	833 m	832 m	832 s	
810 w		804 vw	805 w	806 vw	807 w	5(γC–D)
796 w		789 w	790 w	799 w	790 w	18b′(αC–D)
771 w	775 mw	772 w	774 w	777 w	770 vw	18b(αC–D)
		760 vwsh	760 vwsh		762 vw	5′(γC–D)
731 ms	730 m	732 ms	733 ms	731 ms	732 ms	4(γring)

TABLE III (*continued*)

Mn	Fe	Co	Ni	Cu	Zn	Assignment
726 ms				722 m	725 m	6b′(νring)
718 m	719 m	718 mw	718 m		718 ms	4′(γring)
667 vw	680 vw	676 vw	675 vw	687 vw 681 vw	678 vw	10b′(γC–D)
658 wm	657 w	654 wm	654 wm	667 w 658 w	655 w	10b(γC–D)
623 vs	622 s	629 s	629 s	622 vs	629 s	6b(νring) and 10a(γC–D)
		623 vs	623 vs		623 vs	δ(ClO_4)
608 m		610 m	611 m	617 w 606 w	609 m	6a(νring)
583 s	585 s	590 ms	590 ms	597 ms	594 s	1′(νring)
570 s		586 s	586 s	583 s	587 s	11(γC–D)
472 vw	472 vwsh	470 vw	478 vw	477 vw	475 vw	comb
462 vw	464 w	457 vw	458 vw	454 wm	459 vw	comb
444 vw	444 w	446 vw	448 w		443 vw	E(ring scissors)
432 vw	426 vw	431 vw	439 vw	437 vw	430 vvw	Γ(ring shear)
392 w	397 w	400 wm	405 m	403 wm 389 wm	396 m	16b(γring)

TABLE IV

Infrared assignment (4000–350 cm^{-1}) of $[M(phen)_3](ClO_4)_2 \cdot H_2O$ complexes.

Mn	Fe	Co	Ni	Cu	Zn	Assignment
3598 mbr	3604 mbr	3611 mbr	3608 mbr	3608 mbr	3612 mbr	νO–H(H_2O)
3525 mbr	3520 mbr	3521 mbr	3523 mbr	3522 mbr	3509 mbr	
3080 msh	3085 m	3084 msh	3088 msh	3086 msh	3082 msh	23 (νC–H)
3064 m	3063 m	3064 m	3066 m	3065 m	3064 m	43, 22 and 21 (νC–H)
3024 w	3024 w	3022 w	3024 w	3020 w	3022 w	42 and 19 (νC–H)
		2995 w	3000 wsh	3000 wsh	3002 w	41(νC–H)
2924 w	2923 w	2928 vw	2929 w	2931 w	2935 w	comb
	2855 wbr		2860 wbr			
2778 w	2780 vw	2778 w	2778 w	2778 w	2772 w	
2612 vw		2610 w	2619 w	2617 w	2624 wbr	
2508 vw		2510 w	2510 w	2508 w	2512 w	
2462 vw	2460 vw	2463 w	2461 w	2465 w	2462 vw	
		2414 vw	2419 vw	2411 w	2412 w	
2300 vw	2296 vw	2291 vw	2294 w	2294 w	2295 w	
2265 vw	2263 w	2263 w	2265 w	2263 w	2264 w	
2008 wbr	2003 wbr	2010 wbr		2011 wbr	2009 wbr	
1987 wbr	1985 wbr	1986 wbr	1990 wbr	1975 wbr	1975 wbr	
1942 wbr	1943 wbr	1945 w	1948 wbr	1945 wbr	1948 wbr	
1918 wbr	1917 w	1917 mbr	1919 wbr	1919 wbr	1908 wbr	
1810 wbr	1792 vw	1795 w	1819 wbr	1817 vw	1818 w	
1716 w	1711 w	1716 w	1711 w	1715 w		
1708 w		1703 w		1702 w	1700 w	

TABLE IV (*continued*)

Mn	Fe	Co	Ni	Cu	Zn	Assignment
1625 ms	1626 ms	1624 m	1625 m	1623 m	1625 m	18(νring)
1605 w	1603 wm	1604 w	1604 wm	1604 w	1605 w	17(νring)
1592 m	1586 m	1588 msh	1587 ms	1588 msh 1583 ms	1594 w 1585 msh	40(νring)
1578 m	1579 m	1580 s	1581 ms	1578 ms	1580 ms	39(νring)
1518 vs	1518 vs	1517 vs	1516 s	1518 s	1518 s	16(νring)
1496 ms	1494 m	1494 m	1494 ms	1495 ms	1495 ms	38(αC–H)
1451 vw	1455 vw	1460 vw	1461 vw	1456 vw	1454 vw	15(αC–H)
1425 vs	1426 vs	1424 s	1424 s	1426 vs	1425 vs	37(νring) and 14(νring)
	1411 w				1400 m	36(νring)
1375 vw	1372 vw	1376 vw	1378 vw	1376 vw	1377 vw	comb
1342 m	1342 m	1339 m	1339 ms	1339 ms	1339 m	13(νring)
1314 vw	1320 wsh	1314 vw	1318 w	1318 w	1319 w	35(νring)
1303 mw	1309 mw	1303 mw	1304 m	1305 m	1303 m	12(νring)
1252 vw	1253 vw	1257 vw	1258 vw	1254 vw	1255 vw	34(αC–H)
1224 m	1225 ms	1222 m	1223 ms	1223 m	1225 m	10(νring)
1209 w	1210 w	1209 w	1210 w	1209 w	1210 w	33(αC–H)
1191 vw	1202 vwsh	1197 vw	1199 vw	1200 vwsh	1195 w	9(αC–H)
1146 s	1146 ms	1147 s	1147 s	1148 s	1148 s	8(αC–H) and 31(αC–H)
1076 sbr	1082 vsbr	1082 vsbr	1088 vsbr	1094 vsbr	1080 vsbr	$\nu_a(\mathrm{ClO_4})$, 30 and 7(νring)
			1037 msh	1035 ms	1033 msh	6(νring)
	1001 wsh	1004 mw	1006 mwsh	1007 w	1011 w	29(νring)
992 w		994 mw	992 m	994 w	1001 w	46(γC–H)
969 w		973 w	973 wsh	975 w	975 w	57(γC–H)
		963 w	962 ww	964 w	965 w	58(γC–H)
929 w	930 w	931 w	931 w	932 w	934 w	$\nu_s(\mathrm{ClO_4})$
902 vw	905 vw	903 vw	904 vw	909 w 900 vw	904 vw	28(νring)
866 m	869 m	868 m	869 m	871 wm 865 m	867 ms	48(νring)
842 vs	845 vs	852 s 849 s 842 s	851 s 848 s 842 s	849 s 842 s	855 s 848 s	5(νring) and 49(γC–H)
	829 msh			831 w	834 wsh	59(γC–H)
806 vw		811 vw		811 vw	811 vw	60(γC–H)
773 mw	782 mw	779 w	777 vw 772 vw	780 w 776 vwsh	782 w 776 wm	50(γring)
763 vwsh	770 wsh	767 w	767 wm	767 wm		61(γring)
728 ssh	732 s	727 ssh		731 ssh		51(γC–H)
723 vs	724 vs	724 vs	723 vs	726 s	725 vs	27(γC–H)
				721 s		4(νring)
642 m	642 m	644 m	646 m 643 m	647 m 639 m	645 m 641 m	26(νring)
623 s	623 s	624 s	623 s	623 s	623 s	$\delta(\mathrm{ClO_4})$

TABLE IV (*continued*)

Mn	Fe	Co	Ni	Cu	Zn	Assignment
556 vw	560 w	558 vw	559 vw	557 vw	558 w	3(νring)
543 vw	548 vwsh	546 vw	547 vw	546 vw	547 vw	comb
527 vw	531 wm 526 wm		529 vvw		539 vw	comb
512 vw	511 vw	511 vw	511 vw	511 vw	512 w	52(γring)
500 vw	500 vw			507 vwsh	500 vwsh	63(γring)
477 vw	477 vw	482 vw	485 vw	489 vw 478 vw	482 vw	25(νring)
457 vw	457 vw	458 vw		458 vvw	458 vvw	53(γring)
438 vw	438 vwsh	441 vw	446 vw		437 vw	24(νring)
421 m	426 m	425 wm	426 wm	422 wm	423 m	2(νring)

TABLE V

Infrared assignment (4000–350 cm^{-1}) of [M(phen-d_8)$_3$](ClO$_4$)$_2$·H$_2$O complexes.

Mn	Fe	Co	Ni	Cu	Zn	Assignment
3615 wbr	3600 wbr	3615 wbr	3611 wbr	3603 wbr	3614 wbr	νO-H(H$_2$O)
3481 wbr	3524 wbr	3525 wbr	3521 wbr	3519 wbr	3479 wbr	
2966 wm	2968 w	2966 w	2960 vw	2958 vw	2963 w	comb
2925 w	2924 w	2923 w	2928 w	2922 w	2925 w	
2880 wbr		2858 vw	2860 vw	2854 w	2885 wbr	
2780 w	2780 w	2778 w	2781 w	2780 vw	2783 w	
			2577 w	2575 vvw	2572 vvw	
	2460 vvw	2462 vw	2463 w	2460 vvw	2463 vvw	
2309 w	2307 w	2304 w	2306 w	2305 w	2306 w	23(νC–D)
2284 w	2290 w 2277 w	2283 w	2280 w	2280 w	2290 w	22 and 45(νC–D) 21 and 43(νC–D)
2270 wsh	2270 wsh	2266 w	2264 w	2268 wsh	2275 w	comb
2022 w	2020 wbr	2019 wbr	2019 wbr	2016 wbr	2023 wbr	
	1918 vw	1915 w	1920 w	1922 w		
1792 vw	1797 w		1804 w	1802 vw		
1716 w	1706 wbr	1735 wbr	1728 w	1718 vw	1716 w	
1685 vw		1686 vw	1680 vwbr	1682 vw	1685 vw	
1650 vw		1649 vw	1650 w	1649 w	1652 w	
1611 wbr	1616 wbr	1622 wbr	1622 wbr	1629 vw	1613 w	
1599 m	1604 w	1601 wm	1601 w	1600 w	1601 wm	18(νring)
1586 m	1588 m	1586 m	1588 m	1590 m	1589 m	40(νring)
1553 vw	1551 s	1551 s	1551 s	1553 s	1555 s	17(νring) and 39(νring)
1474 vs	1474 s	1473 vs	1474 vs	1474 vs	1476 vs	16(νring)
		1446 vw	1443 vw		1448 vw	comb
1431 s	1431 s	1431 s	1431 s	1431 s	1431 s	38(αC–D)
1421 ms				1422 m	1425 mw	15(αC–D)
1398 mw					1398 m	

TABLE V (*continued*)

Mn	Fe	Co	Ni	Cu	Zn	Assignment
1388 w	1386 w	1387 w	1388 w	1388 w	1389 w	14(νring)
	1365 w	1366 vw	1369 vw	1368 vw	1370 vw	comb
1342 vs	1341 vs	1344 vs	1345 vs	1344 vs	1346 vs	37(νring)
1320 wsh		1326 msh	1329 wsh		1322 w	36(νring)
1304 m	1308 m	1307 m	1307 m	1307 m	1307 m	13(νring)
	1269 wsh			1275 w		comb
1262 s	1262 ms	1263 ms	1264 ms	1263 s	1263 s	35(νring)
1215 mw	1222 w				1219 w	comb
1168 w	1165 w	1168 w	1160 w	1168 w	1169 w	12(νring)
1098 vsbr	1093 vs	1129 msh 1098 vsbr	1126 ssh 1094 vsbr	1128 ssh 1099 vsbr	1130 ssh 1100 vsbr	$\nu_a(ClO_4)$
1037 s	1037 ssh	1036 s	1036 m	1037 s	1037 s	34(αC–D)
1023 s 1013 m	1020 s	1023 s	1023 s	1022 s	1024 s 1014 m	33(αC–D)
976 s	974 ms	975 ms	975 ms	976 s	977 s	10(νring)
947 vw		946 vw	945 vw	946 vw	947 vw	comb
934 w	928 w	932 w	931 w	932 w	935 w	$\nu_s(ClO_4)$
894 s	892 ms	892 s	893 s	898 ms 892 ms	895 ms	9(αC–D)
870 m	·869 w	870 w	871 vw	870 vw	871 m	31(αC–D)
853 m		854 m	854 m	854 m	854 m	8(αC–D)
840 w		833 w	834 w	836 w	838 w	30(νring) and 7(νring)
816 w	815 m	818 w	818 w	818 vw	817 w	6(νring) and 29(νring)
793 m	782 m	790 m	789 m	792 m 787 m	792 s	5(νring)
772 vw		769 vw	767 vw	768 vw	772 vw	46(γC–D)
761 vw					761 vw	58(γC–D)
750 vw					750 vw	48(γC–D)
735 m	730 m	733 m	733 mw	732 mw	736 wm	28(νring)
722 m	722 msh	722 m	722 mw	721 w	722 w	48(γring)
691 s	694 s	692 s	694 s	699 s 689 s	692 s	27(νring)
675 vw	677 wsh			674 vw	673 vw	60(γC–D)
667 vw	663 w	668 vw	667 vw	669 vw 662 w	667 vw	4(νring)
640 s	636 s	639 s	639 s	638 s	637 s	49(γC–D)
		634 m	632 s	630 s	631 ssh	50(γring)
623 s	621 vs	623 s	623 s	623 s	624 s	$\delta(ClO_4)$
594 ms	590 ms	596 ms	595 s	592 s	595 s	51(γC–D)
541 w	542 w	540 vw	540 vw	541 vw	543 w	26(νring)
482 vw	494 w 478 w	482 vw	483 vw	483 vw 471 vw	483 vw	25(νring)
453 w	459 w	458 w	461 w	460 w	457 w	52(γring)
409 m	413 w	412 m	413 m	411 m	410 m	2(νring)

TABLE VI
Far-infrared assignment (650–50 cm^{-1}) of [M(bipy)$_3$](ClO$_4$)$_2$ complexes and their perdeuterated analogues.

	bipy		Mn		Fe			Co		Ni			Cu			Zn			Assignment	
	-d_0	-d_8	-d_0	-d_8	-d_0	-d_8	$\Delta^{54\,57}$Fe[a]	-d_0	-d_8	-d_0	-d_8	$\Delta^{58\,62}$Ni[a]	-d_0	-d_8	$\Delta^{63\,66}$Cu[a]	d_0	-d_8	$\Delta^{64,57}$Zn[a]	Previous[a]	This work
6a	620	(603)	623 s	(623 vs)	623 s	(622 vs)		623 s	(623 vs)	623 s	(623 vs)		623 s	(623 vs)		623 s	(623 vs)			δClO$_4$
6b′	614	(728)												(617 w)						
				(608 m)		(masked)			(610 m)		(611 m)						(609 m)			6α(νring)
														(606 w)						
			550 vw	(472 vw)	550 vw	(472 vwsh)		550 vw	(470 vw)		(478 vw)		550 vw	(477 vw)			(475 vw)			comb
													498 w							
				(462 vw)	497 w	(464 w)		481 w	(457 vw)	483 w	(458 vw)			(454 wm)		494 w	(459 vw)			comb
													481 w							
Ε	440	(414)	467 w	(444 vw)	475 w	(444 w)		465 w	(446 vw)	465 w	(448 w)			(–)		478 w	(443 vw)			Ε(ring scissors)
Γ	413	(385)		(432 vw)	456 w	(426 vw)		458 vw	(431 vw)	458 vw	(439 vw)		458 w	(437 vw)		459 w	(430 vvw)			Γ(ring shear)
													441 m	(403 wm)						
16b	415	(388)	424 w	(392 w)	438 wsh	(397 w)		439 m	(400 wm)	439 m	(405 m)					428 ms	(396 m)			16b(γring)
													423 m	(389 wm)						
																			ligand A	
													410 ms	(376 msh)						
16a	403	(369)	412 m	(364 ms)	418 ms	**(368 ms)**	**(+0.1)**	413 ms	(365 ms)	413 ms	(366 s)					413 s	(364 s)			16a(γring)
					382 wm		**(+6.0)**						393 msh	(367 ms)						
			365 wsh		**372 w**	**(353 mw)**	**(+5.2)**	365 wsh	(–)	361 w	(345 w)	(–0.6)	365 vw	(–)	(+0.2)	365 vw	(–)		ligand B	comb
													357 vw		(+0.1)					
6a′	330	(315)	355 w	(343 w)		(325 w)		356 w	(345 w)					(352 wm)		358 vw	(355 wsh)	(+0.5)		6a′ (νring)
													349 w		(+0.2)					
										293 ms	**(289 m)**	**(+7.1)**	**286 m**	**(279 m)**	**(+2.7)**					
			280 vw	(275 vw)	**285 m**	**(285 m)**		**280 wm**	**(275 wm)**	**281 m**	**(276 m)**	**(+5.4)**	**271 m**		**(+1.3)**	**262 w**	**(245 w)**	**(+0.3)**	ligand C	νM-N + comb
														(264 wm)						
								264 m	**(257 wm)**	**266 w**	**(264 w)**	**(+7.3)**	**266 msh**		**(+2.0)**					
16b′	236	(210)	(masked)		247 wsh	*(240 wbr)*	*(–0.6)*	**249 w**	(–)	256 wsh	(236 w)		255 w	(237 w)	(+0.0)	248 wsh	(232 wmsh)	(+0.0)	ligand D	16b′ (γring)
			241 ms	**(239 m)**	*241 w*			**231 w**	**(229 w)**							**235 ms**	**(223 ms)**	**(+2.5)**		
			206 wm	**(204 wm)**									*217 w*	*(204 w)*	*(+0.0)*					νM-N
								206 vw	*(–)*	*215 vw*	*(200 vw)*	*(+1.0)*								+
													209 wsh	*(198 w)*	*(+0.0)*				ligand E	δNMN
			190 w	**(179 vwsh)**	*192 w*	*(184 w)*	*(+0.0)*			*183 w*	*(174 vwsh)*		*199 wm*	*(189 w)*	*(+0.8)*	**188 m**	**(180 mw)**	**(+3.5)**		
B	165	(149)	169 w	(171 w)	165 vw	(–)		175 wsh	(169 w)	177 vvw	(170 w)		175 wm	(164 w)	(+0.0)	170 w	(171 wsh)	(+0.1)		B (ring shear)
																			ligand F	
								166 w	*(160 vw)*	*162 w*	*(154 w)*	*(+0.5)*	*163 wm*	*(154 wm)*	*(+0.0)*	*161 vw*	*(154 vw)*			
			150 wsh	*(139 wm)*	*149 vw*	*(143 w)*		*150 w*	*(143 w)*	147 w	(–)		*151 vw*	*(–)*		*145 vw*	*(139 w)*			δNMN
			140 wsh	*(133 wsh)*									*138 vw*	*(130 wsh)*		*125 vvw*	*(–)*			
Δ	117	(99)	118 vvw	(–)	110 vw	(100 wsh)			(–)	116 wsh	(–)		116 w	(107 wsh)		109 vw	(–)			Δ (ring scissors)
Z	95	(66)		(–)	99 w	(84 w)			(89 wsh)	95 vwsh	(90 wsh)		98 wm	(90 wm)		95 wsh	(–)			Z (i. rotation)
			82 wsh	*(83 wsh)*	*79 wsh*	*(75 w)*		*83 wsh*	*(80 wsh)*	*82 w*	*(80 wsh)*			*(83 wm)*		*80 wsh*	*(78 wsh)*			δNMN or lattice
			67 w	(69 w)	66 w	(65 w)		68 w	(69 m)	67 w	(68 m)		65 w	(66 wm)		67 w	(69 m)			
																				lattice
			56 wsh	(56 wsh)	60 wsh	(–)		59 wsh	(57 wsh)	59 wsh	(59 wsh)		56 w	(–)			(–)			

[a] From Nakamoto and his co-workers.[5,6,9,17] Bold face = M-N stretch, italics = M-N bend. *N.B.* -d_8 bands at 590 cm^{-1} (medium strong) and 585 cm^{-1} (strong) not included as they arise from -d_0 bands (modes 1′ and 11) above 630 cm^{-1} (see Tables II and III).

TABLE VII

Far-infrared assignment (650-50 cm^{-1}) of [M(phen)$_3$](ClO$_4$)$_2$ complexes and their perdeuterated analogues.

	phen $-d_0$	phen $-d_8$	Mn $-d_0$	Mn $-d_8$	Fe $-d_0$	Fe $-d_8$	$\Delta^{54\,57}$Fe[a]	Co $-d_0$	Co $-d_8$	Ni $-d_0$	Ni $-d_8$	$\Delta^{58\,62}$Ni[a]	Cu $-d_0$	Cu $-d_8$	$\Delta^{63\,66}$Cu[a]	Zn d_0	Zn $-d_8$	$\Delta^{64\,57}$Zn[a]	Assignment Previous[a]	Assignment This work
																	(624 s)			
			623 s	(623 s)	623 s	(622 s)		624 s	(623 s)	623 s	(623 s)		623 s	(623 s)		623 s				δClO$_4$
26	623	(536)															(595 s)			
62	605	(507)	556 vw	(541 w)	560 w	(542 w)		558 vw	(540 vw)	559 vw	(540 vw)		557 vw	(541 vw)		558 w	(543 w)			3(νring)
3	552	(536)	543 vw	(−)	548 vwsh	(−)		546 vw	(−)	547 vw	(−)		546 vw	(−)		547 vw	(−)			comb
					531 wm															
			527 vvw	(−)		(−)			(−)	529 vvw	(−)					531 vw	(−)			
					526 wm															
52	509	(444)	512 vw	(453 w)	511 vw	(469 vw)		511 vw	(458 w)	511 vw	(461 w)		511 w	(460 w)		512 w	(457 w)			52(γring)
25	499	(480)	500 vw			(495 vw)			(−)		(−)		507 vwsh	(−)		500 vwsh	(−)			63(γring)
63	499	(428)											489 vw	(483 vw)						
			477 vw	(482 vw)	484 vw	(482 w)		482 vw	(482 vw)	485 vw	(483 vw)					482 vw	(483 vw)			25(νring)
													478 vw	(471 vw)						
53	457	(369)	457 vw	(369 vw)	464 vw	(364 vw)		458 vw	(370 vvw)		(372 vvw)		458 vvw	(372 vvw)		458 vvw	(372 vvw)			53(γring)
24	427	(399)	438 vwsh	(masked)	439 vw	(masked)		441 vw	(masked)	446 vw	(masked)			(masked)		437 vw	(masked)	(+0.0)		24(νring)
																			ligand A	
64	411	(350)	421 m	(409 m)	426 m	(437 m)		425 wm	(412 m)	426 m	(413 m)	(−0.1)	422 wm	(411 m)		423 m	(410 m)	(+0.0)		2(νring)
2	402	(385)	394 vvw	(369 vw)	(−)	**(398 w)**	(+4.4)	406 vw	(370 vvw)	395 vw	(372 vvw)		392 vw	(372 vvw)			(372 vvw)			64(γring)
			366 vvw	(−)	**360 vvw**	**(363 w)**	(+6.3)		(−)	366 vvw	(−)			(−)			(−)			
																				comb
				(−)		(339 w)			(−)	338 vvw	(−)		334 vvw	(−)			(−)			
65	253	(254)												(306 vw)						
			276 w	(260 wm)	293 m	(281 m)	(+0.0)						301 w		(+0.5)	285 wm	(271 mw)	(−0.5)	ligand B	65(γring)
								288 m	**(275 m)**	**300 m**	**(288 m)**	(+2.3)		(286 w)						
54	245	(203)		(−)	271 w	(237 wm)	(−0.6)						286 wm	(273 w)	(+0.2)	255 vw	(241 w)			54(γring)
										258 wm		(+3.9)	**267 w**	**(255 w)**	(+1.5)				ligand C	
											(247 w)									νM-N
									(239 wm)	**246 wm**		(+2.8)		**(236 vw)**						
								237 m					**246 wm**		(+2.0)					
1	203	(229)	236 w	(−)	244 w	(220 wm)	(+0.0)		(217 w)	236 wsh	(219 w)	(+0.9)		**(217 w)**		242 w	(217 w)	(+0.0)		1(νring)
			219 m	**(217 m)**	*212 mw*	*(198 wsh)*	*(+0.2)*													
			200 wm	**(201 wsh)**	*192 wsh*	*(185 wsh)*	*(+0.1)*			*(−)*	*(−)*	*(−0.5)*	*(−)*	*(191 vw)*	*(+0.0)*	**192 m**	**(191 m)**	**(+4.0)**		νM-N + δNMN
					175 vw	*(−)*	*(+0.0)*	*179 w*	*(170 vw)*	*189 w*	*(178 w)*	*(−0.5)*	*180 wm*	*(172 mw)*		**176 w**	**(170 vw)**	**(+3.0)**	ligand D	
66	144	(150)	159 wsh	(151 wsh)	155 vwsh	(144 w)		153 w	(143 vw)	160 w	(152 vw)	(+0.5)				159 w	(149 vw)	(+0.0)		66(γring)
			147 w	*(139 w)*									*147 w*	*(141 mw)*	*(+0.0)*	*144 w*	*(143 wsh)*			
																			ligand E	δNMN
														(135 mw)						
55	122	(116)		(−)		(117 w)		127 vwsh	(123 vw)	136 vw	(128 vw)			(129 wsh)			(−)			55(γring)
				(−)	*117 wbr*	*(103 w)*		(−)	*(108 vwsh)*	*109 vw*	*(105 vwsh)*		*105 vw*	*(108 vwsh)*		*109 vw*	*(107 vw)*			
																				δNMN
			80 wsh	*(90 wsh)*	*77 w*	*(78 w)*		*76 wm*	*(72 wsh)*	*76 w*	*(72 w)*		*72 wsh*	*(77 mw)*		*78 wbr*	*(78 w)*			
			70 w	(77 w)	66 w	(62 wsh)		63 w	(65 w)	65 w	(62 wsh)		68 w	(69 mw)		65 wsh	(59 wsh)			lattice
			54 w	(55 wsh)					(55 wsh)		(−)			(−)			(−)			

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[a] From Nakamoto and his co-workers.[5,6,9,17] Bold face = M–N stretch, italics = M–N bend. *N.B.* $-d_8$ band at 595 cm^{-1} (strong) is not included as it arises from $-d_0$ band (mode 51) above 630 cm^{-1} (see Tables IV and V).

The spectra reveal that the bands which arise from a common origin within the localized symmetry of the ligand (*e.g.*, the A_1 and B_1 or the A_2 and B_2 twin components of the pyridyl ring vibrations in *cis*-bipy) are not completely resolved into the full number of components expected for the D_3 complex (*e.g.*, the four components of the pyridyl ring vibrations, A_1, A_2 and $2E$). With the exception of the Cu(II) complexes, only six bands show splitting in the tris(bipy) metal complexes, modes 14(-d_0), 6b(-d_0), 5′(-d_0), 15′(-d_8), 12(-d_8) and 6a(-d_8), while four are split in the phen analogues: modes 50(-d_0), 40(-d_0), 33(-d_8) and 15(-d_8). This weak splitting of the localized ligand symmetry is typical of the tris(bipy) metal complexes.[10]

In both series of metal(II) complexes, several ligand bands show metal sensitivity which follows the Irving–Williams sequence.[18] This metal sensitivity may be explained by comparison with the metal-sensitive ligand vibrations in M(II) complexes with pyridine, for which the planar ring modes 12, 8a, 6a and 1 and the out-of-plane ring mode 16b have long been recognized as being strongly metal-sensitive, while the planar ring modes 19a and 19b, the out-of-plane ring mode 4 and the C–H modes 15 and 5 are lightly metal-sensitive.[19–23] The combination band at *ca* 1640 cm^{-1} (6a + 1) is metal-sensitive due to its components.[23] This metal sensitivity is a result of kinematic coupling with the M–N vibrations.[19,23] The nature and extent of this coupling may be comprehended by comparing it with the coupling experienced in pyridine *N*-oxide (pyO)[24] or in a mono-substituted benzene,[25] since the same ring modes reflect either strong or weak N–O or C–X sensitivity.

In bipy and its -d_8 analogue, several ring modes show metal sensitivity: 19a, 19a′, 19b(-d_0), 16b, 16b′, 16a, 14(-d_0), 12(-d_0), 12′, 8b, 8b′, 6a(-d_8), 6b(-d_0), 1 and 1′. Five C–H bends, modes 18b, 15(-d_0), 15′(-d_0), 10b(-d_8), and 9b(-d_8), and three C–H stretches, 3070 cm^{-1} (degenerate vibration) and 3080 cm^{-1} (mode 20b) show metal sensitivity. Three of the non-benzenoid inter-ring vibrations, modes B(-d_0), Γ(-d_8) and E(-d_8) show metal sensitivity. The poor resolution of the far-infrared prevents an examination of the metal sensitivity of the two inter-ring modes of lowest frequency. The metal sensitivity of these ligand modes may be compared with their corresponding N–O and inter-ring sensitivity in 2,2′-bipyridine-*N*,*N*′-dioxide.[15] The loss or acquisition of metal sensitivity on deuteration reflects a change in the kinematic coupling and is similar to the loss of metal sensitivity by mode 6a in py-d_5.[22]

Kinematic coupling between the ligand modes and the M–N vibrations in the phen complexes is not as extensive, showing fewer metal sensitive bands. Metal sensitive ring modes in the phen complexes are modes 65, 54, 52(-d_8), 28(-d_0), 25, 24(-d_0), 12(-d_0), 5(-d_8), 4(-d_g) and 2(-d_8). One C–H stretch (mode 23), two planar C–H bends (modes 34 and 9) and one out-of-plane C–H bend (mode 48) show metal sensitivity in the phen-d_0 complexes.

With the Jahn–Teller distortion experienced by the Cu(II) complexes, the localized symmetry of the ligand is lowered to yield two different ligand environments, thereby affording the potential for splitting of the ligand bands. From Tables II and III a number of such split bands are observed in the complexes with bipy-d_0 and bipy-d_8, including mode 6b(-d_0) which accounts for the splitting of the 625, 660 cm^{-1} bipy doublet noted by Inskeep.[1] Those bands which show this splitting are generally metal-sensitive. It is also of interest that the inter-ring stretch, mode A(-d_0) shows splitting as a result of Jahn–Teller distortion.

The $[Cu(phen)_3](ClO_4)_2$ complex shows only three split bands, namely modes 48 (αC–H), 28 (νring) and 25(νring) (Table IV). Since the infrared spectrum of this complex is extremely rich, it is not surprising that in the absence of a complete vibrational assignment this evidence for tetragonal distortion was overlooked. The phen-d_8 complex shows twice as many bands which are sensitive to tetragonal splitting; these are modes 64(νring), 27(νring), 9(αC–H), 5(νring) and 4(νring). Again, these are generally metal-sensitive bands.

Finally, of the fifteen metal–ligand vibrations, three infrared active M–N stretches (A_2 and $2E$) and four M–N bends (A_2 and $3E$) are theoretically expected for D_3 symmetry, while the full six stretches ($3A$ and $3B$) and nine bends ($5A$ and $4B$) are expected for the tetragonal Cu(II) complexes. Site and correlation field splitting of the bands into several components is not expected in these complexes because of the large size of the ligands.[26]

The assignments of the metal–ligand vibrations are rendered difficult because of the presence in both series of low lying ligand bands within this region, as well as resulting from the sensitivity of the metal–ligand bands to the crystal field stabilization energy (CFSE). The assignments below 625 cm^{-1} of the M(II) tris-bipy and tris-phen complexes are given in Tables VI and VII. These have been based upon the assignment of the ligand bands, upon their metal sensitivity and upon deuteration and metal isotope sensitivity.

The metal–nitrogen stretches are found in the region 400 to 180 cm^{-1} for both series and, with the exception of Fe(II), follow the Irving–Williams sequence (namely Mn < Fe < Co < Ni < Cu > Zn).[18] The M–N stretches for Fe(II) are some 90 to 150 cm^{-1} higher than the other metals as a result of their greater CFSE, being low spin complexes.[3]

Within the bipy complexes, all three of the expected infrared active M–N stretches are observed. Their assignment is complicated by the presence in this region of two ligand bands at *ca* 355 cm^{-1}(-d_0) and at *ca* 250 cm^{-1}(-d_0) (being modes 6a′ and 16b′)[15] and of a combination or difference band at 280 cm^{-1}(-d_0) (Table VI). Indeed, mode 6a′ was assigned as a metal-nitrogen stretch by Percy and Thornton because of its metal sensitivity.[3]

In the spectra of the phen complexes, generally only two of the three expected M–N stretches are observed (Table VII). This is probably due to accidental degeneracy with an incomplete resolution of the bands. The presence of twice as many combination bands (at 340 and 370 cm^{-1}) and twice as many ligand bands at 390 cm^{-1}(-d_0), 285 cm^{-1}(-d_0), 260 cm^{-1}(-d_0) and 240 cm^{-1}(-d_0) (being modes 64, 65, 54 and 1, respectively)[16] makes the νM–N assignments more difficult than in the case of the bipy complexes. Consequently, with the stretching frequencies lying below the frequency range that they examined, Percy and Thornton incorrectly assigned the ligand modes 1 and 65 as νM–N for the metals Mn and Zn.[3] A further such difficulty is observed in the Cu(II) complex, for which the bands at 301 cm^{-1} and 286 cm^{-1} may also be considered as possibly highly-coupled νM–N (particularly the former in view of its metal isotope sensitivity) rather than as ligand modes 65 and 54.

The metal–nitrogen bends show less metal sensitivity than the stretches, as shown by the Fe(II) frequencies being only some 30 to 70 cm^{-1} higher than the other metals. These bends are found in two ranges. The highest bends are found between 240 and 140 cm^{-1} in both metal series. In ML_6 *N*-heterocyclic complexes the two lowest δM–N vibrations occur at *ca* 100 cm^{-1} and at *ca* 80 cm^{-1},[27] and since chelation causes the M–N bends to be found at slightly higher frequencies than for monodentate complexes,[28] the lowest δM–N is assigned to the band at 150 and 125 cm^{-1} in the bipy complexes and at 115 to 105 cm^{-1} in the phen complexes. The band at 80 to 70 cm^{-1} (both series), which is the highest lattice vibration, may also mask the lowest δM–N for the Mn and Zn complexes. Of the four δM–N modes expected, two to four are observed depending upon the metal. (For Mn and Zn only two of the bends are clearly identified in both series). The assignments of these bends are complicated by the presence of three ligand modes (modes B, Δ and Z) for bipy, and two ligand modes (modes 66 and 65) for phen (Tables VI and VII).

It is necessary to comment further on the behaviour of the Cu(II) complexes with bipy and phen. Six M–N stretches and nine bends are expected for C_2 symmetry; however, only three stretches and six bends are observed for the $\mathrm{Cu(bipy)_3}^{2+}$ cation and two stretches (with a possible third) and five bends are observed for the $\mathrm{Cu(phen)_3}^{2+}$ cation. It is therefore clear that the splitting of the M–N fundamentals expected for tetragonal distortion does not appear to occur for the stretches, although it does for some of the bends. This may be accounted for by the stretching modes being accidentally degenerate, and hence not fully resolved. Support for this suggestion is obtained from the infrared and Raman spectra of the Zn *tris*-phen complex in which the polarized Raman line at 286 cm^{-1} has a strong infrared counterpart at 288 cm^{-1}, which is evidence that the symmetric and antisymmetric Zn–N stetches are degenerate.[29] The infrared and Raman spectra of the Ru(II) tris-bipy cation reveals the same situation.[10]

In conclusion, the fully deuterated ligand study has enabled a full assignment of the low lying frequencies of the M(II) *tris*-bipy complexes and their phen analogues. It has allowed a more complete assignment of the "ligand vibrations" made by Nakamoto and coworkers[5,6,9] (Tables VI and VII). Indeed, some of the "ligand bands" identified by these authors have been found actually to consist of two ligand modes, (*e.g.*, Ligand A in bipy complexes is more correctly identified as modes 16a and 16b, while for the phen complexes Ligand A consists of modes 2 and 24, and Ligand C is more correctly modes 1 and 54). Of the "ligand bands" previously considered as *activated* ligand vibrations, some have been clearly identified (*e.g.*, Ligand D in the bipy complexes is mode 16b′), while others are identified as actually consisting of two vibrations (*e.g.*, in the bipy complexes Ligand B is identified as being a combination band and mode 6a, with Ligand F consisting of mode B and δM–N, while in the phen complexes Ligand D describes the ligand mode 66 and a δM–N band). Furthermore, some of the bands considered by Nakamoto and coworkers to be *activated* ligand bands are preferentially now assigned as M–N bends (*e.g.*, Ligand E in the bipy complexes and Ligand E in the phen complexes). The two lowest-lying ligand modes in the bipy complexes (modes Δ and Z) and the lowest mode in the phen complexes (mode 55) have been newly identified, being found at frequencies below the range previously investigated. Finally, the present deuteration study in conjunction with previous metal–isotope studies[5,6,9,17] show that the M–N fundamentals are coupled vibrations, corroborating the kinematic coupling behaviour experienced by some of the ligand vibrations.

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REFERENCES

1. R.G. Inskeep, *J. Inorg. Nucl. Chem.*, **24**, 763 (1962).
2. G.C. Percy and D.A. Thornton, *Spectrosc. Lett.*, **3**, 323 (1970).
3. G.C. Percy and D.A. Thornton, *J. Molec. Struct.*, **10**, 39 (1971).

4. G.C. Percy and D.A. Thornton, *J. Molec. Struct.*, **14**, 313 (1972).
5. B. Hutchinson, J. Takemoto and K. Nakamoto, *J. Am. Chem. Soc.*, **92**, 3335 (1970).
6. Y. Saito, J. Takemoto, B. Hutchinson and K. Nakamoto, *Inorg. Chem.*, **11**, 2003 (1972).
7. O.P. Anderson, *J. Chem. Soc., Dalton Trans.*, 2597 (1972).
8. O.P. Anderson, *J. Chem. Soc., Dalton Trans.*, 1237 (1973).
9. J.H. Takemoto, B. Streusand and B. Hutchinson, *Spectrochim. Acta*, **30A**, 827 (1974).
10. O. Poizat and C. Sourisseau, *J. Phys. Chem.*, **88**, 3007 (1984).
11. J.S. Strukl and J.L. Walter, *Spectrochim. Acta*, **27A**, 223 (1971).
12. S. McClanahan and J. Kinkaid, *J. Raman Spectrosc.*, **15**, 173 (1984).
13. N. Neto, M. Muiz-Miranda, L. Angeloni and E. Castellucci, *Spectrochim. Acta*, **39A**, 97 (1983).
14. M. Muiz-Miranda, E. Castellucci, N. Neto and G. Sbrana, *Spectrochim. Acta*, **39A**, 107 (1983).
15. D.A. Thornton and G.M. Watkins, *Bull. Soc. Chim. Belges*, **100**, 221 (1991).
16. D.A. Thornton and G.M. Watkins, *Spectrochim. Acta*, **47A**, 1085 (1991)
17. R.E. Wilde and T.K.K. Srinivasan, *J. Inorg. Nucl. Chem.*, **36**, 323 (1974).
18. H. Irving and R.J.P. Williams, *J. Chem. Soc.*, 3192 (1953).
19. S. Suzuki and W.J. Orville-Thomas, *J. Molec. Struct.*, **37**, 321 (1977).
20. N.N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).
21. N.S. Gill, R.H. Nuttall, D.E. Scaife and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).
22. J.R. Durig, B.R. Mitchell, D.W. Sink, J.N. Willis and A.S. Wilson, *Spectrochim. Acta*, **23A**, 1121 (1967).
23. S. Akyüz, A.B. Dempster, R.L. Morehouse and S. Suzuki, *J. Molec. Struct.*, **7**, 105 (1973).
24. S. Szöke, A. Gelléri and E. Baitz, *Acta Chim.*, **48**, 343 (1966).
25. G. Varsány and S. Szöke, *Vibrational Spectra of Benzene Derivatives*, (Academic Press, New York, 1969).
26. E.D. McKenzie, *Coord. Chem. Rev.*, **6**, 187 (1971).
27. D.M. Adams and W.R. Trumble, *J. Chem. Soc., Dalton Trans.*, 30 (1975).
28. C. Postmus, J.R. Ferraro and W. Wozniak, *Inorg. Chem.*, **6**, 2030 (1967).
29. K. Krishnan and R.A. Plane, *Spectrochim. Acta*, **25A**, 831 (1969).