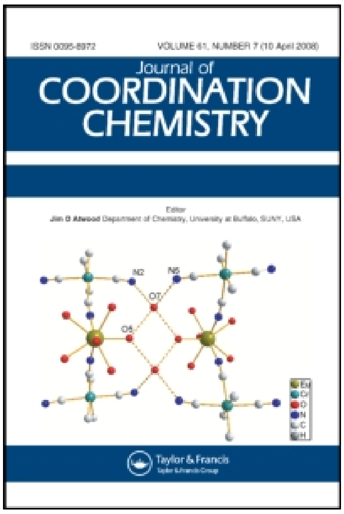

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The Infrared Spectra (4000-50 cm^{-1}) of Complexes of 2,2'-Bipyridine-N,N'-Dioxide and its Perdeuterated Analogue with Metal(II) Perchlorates of the First Transition Series

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THE INFRARED SPECTRA (4000–50 cm^{-1}) OF COMPLEXES OF 2,2′-BIPYRIDINE-*N*,*N*′-DIOXIDE AND ITS PERDEUTERATED ANALOGUE WITH METAL(II) PERCHLORATES OF THE FIRST TRANSITION SERIES

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A full infrared assignment (4000–50 cm^{-1}) for the complexes $[M(bipyO_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$ (M = Mn, Co, Ni, Cu, Zn; bipy = 2,2′-bipyridine-*N*,*N*′-dioxide) and their perdeuterated analogues is presented. Several ligand modes reflect metal sensitivity, with a strong coupling between νM–O and ligand mode 6a in all but the Cu complex. It is proposed that the decoupling of these vibrations in the Cu complex is a result of Jahn–Teller distortion. Attempts to form the Fe(II) complex result in oxidation to Fe(III).

Keywords: Infrared spectra, 2,2′-bipyridine-*N*,*N*′-dioxide, deuteration, metal(II) perchlorates

INTRODUCTION

2,2′-Bipyridine-*N*,*N*′-dioxide ($bipyO_2$) has been quite extensively employed as a ligand,[1] but no isotope spectroscopic study has yet been reported. Several studies of M(II) *tris*-$bipyO_2$ complexes of the metals Mn, Co, Ni, Cu and Zn are to be found in the literature.[2–6] Of these, the only papers to report νM–O assignments are those of Vinciguerra *et al.*[3] and Ahuja and Singh.[5] No assignment of the vibrations below the M–O stretches are to be found in the literature.

$BipyO_2$ coordinates through both oxygens in these complexes, to yield a stable seven-membered chelate ring in which the two pyridyl rings are twisted through a dihedral angle of some 67°.[7] The M–O–N angle in $[Ni(bipyO_2)_3](ClO_4)_2$ is calculated to be 117°[7] {in $[La(bipyO_2)_4](ClO_4)_3$ the M–O–N angle is crystallographically determined to be 123°[8]}, which is typical of an aromatic *N*-oxide. While this angle is generally accepted as evidence for sp^2 hybridization of the oxygen (*i.e.*, the two lone pairs plus the N–O bond pair, with the third lone pair in a *p* orbital available for π-interaction with the pyridine ring) and so indicating a significant contribution of the canonical form (*II*) (Figure 1) in the complex, Ng *et al.*[9] disagree. They note that if the π-interaction is important then the planes of the M–O–N moiety and the pyridine ring should be coincident. Since this orientation is between 34° and 93° for a wide range of pyO complexes which have been crystallographically examined, Ng *et al.* suggested that this is evidence of distorted sp^3 hybridization, resulting from the fact that forcing the M–O–N and pyridine rings into coincidence would maximize the steric interference of the aromatic ring with the other ligands on the metal atom.[9]

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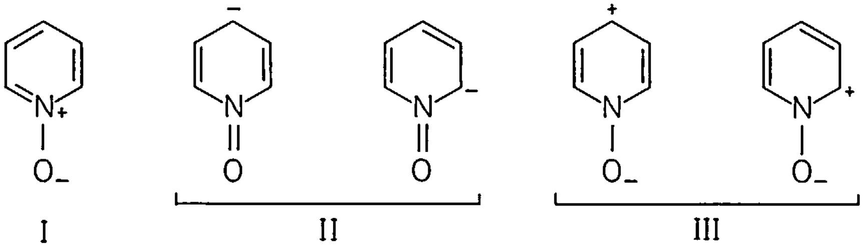

FIGURE 1 Resonance structures of pyridine-*N*-oxide.

Considering the high *s* character of the oxygen orbital,[9,10] delocalization of the second lone pair at the oxygen into the aromatic ring is retarded on the grounds of the poor geometry and the energetics involved. Furthermore, overlap of the second lone pair with the acceptor of the metal atom is considered to be energetically poor since a positive charge on the nitrogen would reduce electron flow from the oxygen.[9,10]

The *N*-oxides are therefore poorer π acceptors and weaker σ donors than their imine parents. Although bidentate bipyO_2 gives rise to a stronger ligand field than that of pyO, it does not have sufficient field strength to cause the spin-pairing that is found for complexes of bipy and phen[4,11] (Table I). Any metal-sensitive vibration in the metal(II) complexes of bipyO_2 is then expected to follow more precisely the Irving–Williams series (Mn < Fe < Co < Ni < Cu > Zn).[12] In particular, the Fe(II) complex is expected to be high spin {as in the complex $[Fe(pyO)_6](ClO_4)_2$}, but we were unable to synthesize this compound (see below).

TABLE I
Literature values of 10*Dq* for several aromatic imines and their *N*-oxides.

	high spin			low spin	
ligand	quinO	pyO	bipyO_2	py	bipy
10*Dq*(cm^{-1})[a]	7900	8400	8600	11500	11500
Reference	[11]	[4]	[4]	[4]	[4]

[a] For Ni^{2+} cation.

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 cm^{-1} 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 16B/D interferometer. The ligands were prepared as previously described.[13]

Preparation of $[M(bipyO_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$ *(M = Mn, Co, Ni, Cu, Zn)*

Two cm^3 of a hot aqueous solution of 0.1 g (0.27 mmol) of the metal perchlorate (as the hydrated salt) was added to a hot solution of 0.15 g (0.81 mmol; 3:1 mole ratio) of 2,2'-bipyridine-*N*,*N*'-dioxide in 5 cm^3 of water, with stirring. On cooling, the precipitate was filtered and washed with 2 cm^3 of cold water. The complex was recrystallized from a minimum amount of hot water and dried over silica gel under reduced pressure. Yields of between 65 and 92% were obtained. Microanalytical data are given in Table II.

The deuterated complexes were prepared as for their -d_0 analogues, using one-half quantities of reactants. Yields of between 70 and 87% were obtained. Microanalytical data are given in Table II.

TABLE II

Microanalyses of $M(II)(ClO_4)_2$ complexes of $bipyO_2$ and bipy-d_8O_2.

		Experimental			Calculated		
Complex	Colour	%C	%H	%N	%C	%H	%N
$[Mn(bipyO_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$[a]	burnt orange	42.40	3.20	9.90	42.62	3.22	9.94
$[Co(bipyO_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$	brick red	43.35	3.10	9.85	42.42	3.20	9.89
$[Ni(bipyO_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$	lime green	42.30	3.15	9.95	42.43	3.20	9.90
$[Cu(bipyO_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$	light green	42.50	3.10	9.90	42.19	3.19	9.84
$[Zn(bipyO_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$	white	42.15	3.20	9.80	42.10	3.18	9.82
$[Mn(bipy\text{-}d_8O_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$[a]	burnt orange	41.60	3.10	9.60	41.43	3.13	9.66
$[Co(bipy\text{-}d_8O_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$	brick red	41.30	3.15	9.65	41.25	3.12	9.62
$[Ni(bipy\text{-}d_8O_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$	lime green	41.40	3.10	9.65	41.26	3.12	9.65
$[Cu(bipy\text{-}d_8O_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$	light green	41.10	3.00	9.65	41.03	3.10	9.57
$[Zn(bipy\text{-}d_8O_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$[a]	white	41.10	3.10	9.65	40.93	3.09	9.55

[a] Light sensitive.

RESULTS AND DISCUSSION

$[Fe(bipyO_2)_3](ClO_4)_2$ has not been reported in the literature and repeated attempts to prepare this complex and its fully deuterated analogue (under nitrogen) were unsuccessful as the infrared spectrum clearly showed oxidation to Fe(II) {two νM–O at 412 cm^{-1} and 380 cm^{-1}; literature 408 cm^{-1} and 377 cm^{-1} for the $[Fe(bipyO_2)_3]^{3+}$ cation[3]}. A further difficulty experienced arose from the ability of the Fe(III) complex to be formed with more than three moles of $bipyO_2$ per mole of iron.[4]

The full vibrational assignments for the metal(II) complexes of $bipyO_2$ and its fully deuterated analogue are based upon the assignments of the free ligand,[13] and are presented in Tables III and IV. The far-infrared assignments (below 625 cm^{-1}) reflecting the deuteration shifts, are presented in Table V.

As was observed for the bipy and phen complexes,[14] the bands arising from a common origin within the localized ligand symmetry are not completely resolved. Except for the Cu(II) complexes, only three bands (these being νN–O, modes 7a' and 7a, and γC–H, mode 11) are split in the $bipyO_2$ complexes, while only one is split in the bipy-d_8O_2 complexes (the νring mode 19b).

TABLE III
Infrared assignment (4000–350 cm^{-1}) of $[M(bipyO_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$ complexes.

Mn	Co	Ni	Cu	Zn	Assignment
3596 mbr 3512 mbr	3592 mbr 3506 mbr	3591 mbr 3480 mbr	3562 mbr 3460 mbr	3596 mbr 3511 mbr	νO-H(H_2O)
3220 vw	3220 vvw		3220 vvw	3220 vvw	comb
3123 m	3123 m	3128 m	3128 m	3125 m	20a(νC-H)
3105 m	3107 m	3092 ms		3109 m	20b(νC-H)
3092 msh	3087 msh		3088 ms	3095 m	20a′ and 20b′(νC-H)
3057 msh	3060 msh	3060 m	3059 m	3060 m	2(νC-H)
3051 m	3045 m			3050 m	2′ and 7b′(νC-H)
3034 mwsh		3038 msh	3038 msh		7b′(νC-H)
2986 vw	2990 w	2988 wsh	2990 w	2988 wsh	comb
2920 vw	2930 w	2930 w	2923 w	2928 w	
2860 vw	2856 w	2856 w	2860 w	2855 w	
2783 w	2788 w	2783 w	2783 w	2782 w	
2733 vw	2730 vw	2732 vw	2730 vw	2735 vw	
2651 w	2638 w	2642 vw	2640 vw	2652 w	
2455 wsh	2464 wsh	2456 wsh	2460 w	2455 w	
2425 w	2418 wbr	2416 w	2410 w	2424 w	
2333 vw	2320 vw	2329 vw	2329 vw	2333 vw	
2266 vw	2263 w	2264 w	2265 w	2267 w	
2046 wm	2036 wm	2039 wm	2033 wm	2042 wm	
2005 wbr	2005 w	2006 w		2008 wbr	
1957 w	1954 w	1956 w	1960 w	1960 wsh	
1918 vw	1918 vw			1918 w	
1842 w	1845 w	1842 w	1848 w	1841 w	
1628 mbr	1626 mbr	1630 mbr	1637 w 1626 mbr	1631 mbr	νO-H(H_2O) and 8a′ (νring)
1605 w	1606 wsh	1605 wsh	1602 w	1604 wsh	8b′(νring) and 8a(νring)
1573 w	1572 w	1574 w	1574 w	1574 w	8b(νring)
1506 wm	1506 w	1505 w	1505 w	1505 w	19a′(αC-H)
1479 s	1474 s	1474 s	1480 ssh 1474 s	1474 s	19a(αC-H)
1441 s	1440 s	1442 s	1440 s	1442 s	19b′(αC-H)
1426 s	1424 s	1425 s	1425 s	1426 s	19b(αC-H)
1370 vw	1375 vw	1370 vw	1375 vw	1368 vw	3′(αC-H)
1313 vw	1317 w	1317 vw	1316 vw	1317 vw	14′(νring)
1293 w	1292 w	1292 w	1290 w	1293 w	14(νring)
1257 ms	1258 ms	1258 ms	1257 ms	1258 ms	A(νinter-ring)
1232 vs 1226 vssh	1231 ssh 1221 vs	1223 vs	1231 vs	1229 s	7a′(νN-O/νring)
1216 vs	1211 vssh 1203 vs	1211 vs	1216 vs 1209 vs	1211 vs	7a(νN-O/νring)
1164 s	1165 s	1163 s		1166 ssh	15′(αC-H)
			1158 s		
	1163 s	1161 s		1163 s	15(αC-H)
	1111 ssh	1111 ssh	1110 ssh	1110 ssh	9b′(αC-H)

TABLE III (*continued*)

Mn	Co	Ni	Cu	Zn	Assignment
1095 vsbr	1090 vsbr	1088 vsbr	1085 vsbr	1083 vsbr	$\nu_a(ClO_4)$ and 9b(αC-H)
	1061 ssh	1060 ssh	1057 ssh	1056 ssh	
	1050 msh	1048 msh	1049 msh	1048 msh	18b'(αC-H)
1032 m	1032 m	1035 m	1033 m	1033 m	18b(αC-H)
1004 w	1005 mw	1003 mw	1004 mw	1003 m	1(νring)
965 wsh			964 w		5'(γC-H)
	962 w	962 w		959 w	
961 m			952 w		5(γC-H)
930 w	930 w	932 w	931 w	932 w	$\nu_s(ClO_4)$
925 wsh	927 wsh	929 w			10b'(γC-H)
890 w	891 vw	889 vw	891 vw	885 vw	10b(γC-H)
849 s	847 s	848 s	848 s	848 s	12(νring/νN-O)
835 s	834 s	835 s	834 s	834 s	12'(νring/νN-O)
787 msh	788 msh	787 msh		786 msh	11'(γC-H)
	780 vs				
779 vs		780 vs			
	776 vs		775 vsbr	775 vs	11(γC-H)
773 vs		776 vs			
	773 vs				
750 w	751 w	752 w	751 w	751 w	1'(νring)
733 m	733 m	733 m	732 w	733 w	4'(γring)
725 ms	726 s	723 ms	723 ms	722 ms	4(γring)
639 w	638 w	638 w	637 w	639 w	comb
623 s	624 s	624 s	623 s	624 s	$\delta(ClO_4)$
584 s	582 s	584 s	582 s	581 s	6a(νring)
559 w	559 w	559 w	559 w	560 w	comb
540 s	542 m	542 m	546 mw	539 ms	6b(νring)
527 m			531 mwsh		6b'(νring)
517 s	518 s	518 s	518 s	518 s	16b and 16b'(γring/γN-O)
481 m	479 m	479 m	479 m	479 m	18a'(αN-O)
452 s	453 s	452 s	452 s	452 s	18a(αN-O)

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

Several fundamentals reflect metal sensitivity: modes 18a(-d_8), 18b(-d_0), 17a, 16b'(-d_8), 14(-d_8), 6a and 6b. The non-benzenoid inter-ring modes Γ, Δ, E and Z also show metal sensitivity in bipyO_2. The inter-ring stretch, mode A, is not metal-sensitive, while the last inter-ring mode, B, is masked by the highest M–O stretch. Two combination bands at *ca* 1940 cm^{-1} (-d_8) and 1840 cm^{-1} (-d_0) also reveal metal sensitivity, which is most probably a result of the fact that one of their components is one of the metal-sensitive fundamentals already mentioned.

The tetragonal Jahn–Teller distortion experienced by the Cu(II) complex with its perturbed localized symmetry of the ligand is reflected by the splitting of the ligand bands 19a(-d_0), 19b(-d_8), 8a'(-d_0), 7a, 7a'(-d_8), 8a'(-d_0) and Γ (Tables III and IV).

The assignment of the M–O fundamentals is rendered difficult by the presence of eight ligand modes below 400 cm^{-1} [13] (Table V). Vinciguerra *et al.* assigned two bands to νM–O in the infrared spectra of the metal(II) complexes, one found between 392 and 355 cm^{-1} and the other between 354 and 430 cm^{-1}.[3] They made this assignment on the (incorrect) basis that no ligand band is observed between the frequencies 434 and 340 cm^{-1}. Ahuja and Singh[5] only considered the higher frequency band as being suitable for assignment to νM–O since they observed a ligand band at *ca* 360 cm^{-1} which they considered to give rise to the band between 354 and 340 cm^{-1} in the complex spectra (this ligand band has been identified in the present work as mode 6a[13]).

TABLE IV

Infrared assignment (4000–350 cm^{-1}) of $[M(bipy\text{-}d_8O_2)_3](ClO_4)_2\cdot 1\frac{1}{2}H_2O$ complexes.

Mn	Co	Ni	Cu	Zn	Assignment
3597 wbr	3593 wbr	3593 wbr	3596 wbr	3593 wbr	νO–H(H_2O)
3512 wbr	3506 wbr	3506 wbr	3512 wbr	3509 wbr	
3135 vw	3150 vw	3160 vw	3152 vw	3150 vw	comb
	2950 vw		2956 vw	2950 vw	
2917 vw	2923 w	2920 vw	2924 w	2920 w	
	2852 w		2846 w	2850 w	
2778 vw	2779 w	2771 vw	2778 w	2776 vw	
2503 vw	2496 w	2497 w	2500 w	2504 w	
2323 wm	2323 wm	2325 wm	2324 w	2324 w	20a(νC–D)
2309 wsh	2308 w	2307 wm	2309 wm	2309 w	20b and 20a′(νC–D)
2290 wsh	2285 wsh	2287 wm	2290 w	2285 wsh	20b′ and 2′(νC–D)
2283 w	2280 wm	2279 wm	2281 w	2281 w	2 and 7b(νC–D)
2185 w	2185 vw	2190 vw			comb
	2110 vw	2113 vw	2115 vw	2119 w	
2045 w	2040 wsh	2045 wsh	2040 wsh	2048 w	
	2020 w	2018 w	2022 w	2016 w	
	1944 w	1948 w	1946 w	1943 w	
1920 w		1916 w	1920 w	1917 w	
1628 ms	1626 ms	1627 ms	1626 ms	1627 ms	δO–H(H_2O) and 8a′(νring)
1575 w	1574 w	1574 w	1574 w	1575 w	8a and 8b(νring)
1542 m	1543 m	1544 m	1543 m	1544 m	8b(νring)
1438 mw	1438 mw	1439 mw	1439 mw	1439 m	19a′(νring)
1391 wsh	1391 vwsh	1390 vwsh	1392 wsh	1393 wsh	comb
1370 ms	1369 s	1369 s	1370 s	1370 s	19b′(νring)
1350 s	1350 vs	1351 vs	1349 s	1351 s	19a(νring)
1330 ssh	1321 vs	1323 vs	1332 ssh	1332 ssh	19b(νring)
1324 s			1322 vs	1326 vs	
1310 w				1308 mwsh	14′(νring)
1224 mw	1226 mw	1227 wm	1226 wm	1226 wm	14(νring)
1207 s	1207 ms	1208 ms	1207 ms	1208 ms	A(νinter-ring)
			1187 msh		
1179 vs	1174 ssh	1176 ssh			7a′(νN–O/νring)
			1172 vs	1173 vs	
1175 vs	1166 vs	1173 vs	1166 vs		7a(νN–O/νring)
1110 ssh		1109 ssh	1111 ssh	1113 ssh	$\nu_a(ClO_4)$ and 3′(αC- D)
1098 vsbr	1095 vsbr	1094 vsbr	1094 vsbr	1094 vsbr	
			1080 vssh	1084 vssh	
		1056 ssh	1050 mssh	1055 ssh	

TABLE IV (*continued*)

Mn	Co	Ni	Cu	Zn	Assignment
1024 w	1025 mwsh		1025 wsh		3(αC–D)
1010 ms	1010 ms	1010 ms	1010 ms	1009 ms	1(νring)
929 w	930 w	930 w	930 w	930 w	$\nu_s(\mathrm{ClO_4})$
926 vwsh	926 w	926 w	926 wsh	926 wsh	
881 s	879 s	880 ssh	880 s	880 s	9b′(αC–D)
874 s	873 s	873 s	874 s	874 s	9b(αC–D)
864 w	864 w	864 w	864 w	864 w	15′(αC–D)
850 w	850 w	850 w	850 w	850 w	15(αC–D)
835 m	835 ms	833 m	835 m	835 m	5(γC–D)
824 w	824 w	825 w	824 w	825 w	18b′(αC–D)
791 s	788 s	789 s	788 s	789 s	18b(αC–D)
776 vs	776 s	776 s	776 vs	776 vs	12(νring/νN–O)
765 s	766 m	766 m	766 ms	766 ms	12′(νring/νN–O)
738 m	740 w	738 w	739 w	740 w	10b′(γC–D)
723 m	723 w	723 w	722 w	723 w	10b(γC–D)
688 wm	688 wm	687 wm	688 wm	687 wm	1′(νring)
650 wm	651 wm	650 wm	651 wm	651 wm	10a(γC–D)
640 wsh	639 w	639 w	639 vw	637 w	10a′(γC–D)
625 vs	624 vs	622 vs	622 vs	622 vs	$\delta(\mathrm{ClO_4})$ and 4(γring)
619 ssh	619 ssh	617 ssh	616 ssh	617 ssh	11(γC–D)
611 s	611 s	609 s	611 s	611 s	4(γring)
566 ms	566 ms	565 s	566 s	564 s	6a(νring)
556 vs	556 vs	557 vs	556 vs	556 vs	11′(γC–D)
509 s	505 ssh	506 ssh		507 s	6b(νring)
			504 s		
501 s	502 s	501 s		499 s	16b(γring) and 6b′(νring)
472 s	477 wm	476 wm	477 wm	475 wm	16b′(νring)
444 vw	443 vw	443 vw	443 w	442 vw	18a′(αN–O)
419 s	420 s	419 s	417 s	416 s	18a(αN–O)

From the infrared spectra (Table V) and in agreement with the two previous assignments, the strong band in the range 395 to 357 $\mathrm{cm^{-1}}$ is assigned to a metal-oxygen stretch. This stretch masks the inter-ring torsion, mode B.

The ligand mode 6a is tentatively assigned to the band of medium to strong intensity (sometimes appearing as a shoulder on the higher νM–O band) between 353 and 326 $\mathrm{cm^{-1}}$. It is clearly metal-sensitive and must therefore be coupled with νM–O. Evidence for the assignment of this band to 6a is found in the frequency for the Cu(II) complex. The medium band at 326 $\mathrm{cm^{-1}}$ is at a much lower frequency than is found in either the Mn or Zn complex, and therefore in complete disagreement with the CFSE order expected from a M–O stretch.[15] The low frequency of the band at 326 $\mathrm{cm^{-1}}$ in the Cu(II) complex may be explained by the fact that Jahn–Teller distortion leads to a change in the coupling between νM–O and 6a compared with the other complexes. This also results in a much higher decoupled M–O stretch in Cu (at 395 $\mathrm{cm^{-1}}$) in comparison with the other metals. However, an alternative explanation is that both the strong band at 395 $\mathrm{cm^{-1}}$ and the medium band at 326 $\mathrm{cm^{-1}}$ are a result of "splitting" of the highest νM–O as a result of Jahn–Teller distortion of the

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

	bipyO$_2$		Mn		Co		Ni		Cu		Zn		
	-d_0	-d_8'	-d_0	-d_8	-d_0	-d_8	-d_0	-d_8	-d_0	-d_8	-d_0	-d_8	Assignment
			623 s	(625 vs)	624 s	(624 vs)	624 s	(622 vs)	623 s	(622 vs)	624 s	(622 vs)	δ(ClO$_4$)
6a	581	(556)	584 s	(566 m)	583 s	(566 ms)	584 s	(565 s)	582 s	(566 s)	581 s	(564 s)	6a(νring)
			559 w	(–)	559 w	(–)	559 w	(–)	559 w	(–)	560 w	(–)	comb
6b	541	(519)	540 s	(509 s)	542 m	(505 ssh)	542 m	(506 ssh)	546 mw		539 ms	(507 s)	6b(νring)
										(504 s)			
6b′	526	(504)	527 m						531 mwsh				6b′(νring)
				(501 s)		(502 s)		(501 s)				(499 s)	
16b′	516	(481)			518 s		518 s				518 s		16b(γring/γN-O)
			517 s						518 s				
16b	516	(468)		(472 s)		(477 wm)		(476 wm)		(477 wm)		(475 wm)	16b′(γring/γN-O)
18a′	478	(442)	481 m	(444 vw)	479 m	(443 vw)	479 m	(443 vw)	480 s	(443 vw)	479 s	(442 vw)	18a′(αN-O)
18a	466	(432)	452 s	(419 s)	453 s	(420 s)	452 s	(419 s)	452 s	(417 s)	452 s	(416 s)	18a(αN-O)
B	350	(350)	**357 s**	**(345 s)**	**367 s**	**(351 s)**	**377 s**	**(359 s)**	**395 s**	**(379 s)**	**362 s**	**(314 wm)**	νM-O
6a	320	(301)	331 ms	(311 m)	349 mssh	(326 wsh)	353 msh	(335 wsh)	326 m	(305 m)	336 ms	(315 wm)	6a(νring)
						(297 w)		**(300 w)**					
			294 mw	**(278 w)**	**298 mw**		**300 mw**		**299 vw**	**(277 vvw)**	**296 w**	**(227 vw)**	νM-O
						(278 w)		**(282 w)**					
									285 vvw	(–)			
Γ	276	(267)	265 w	(258 w)	268 w	(257 vw)	280 vw	(248 w)			261 w	(255 w)	Γ(ring shear)
									255 w	(246 w)			
17a′	220	(211)	227 vw	(227 vw)		(–)	229 wsh	(–)		(–)		(–)	17a′(γN-O/γring)
17a	214	(204)	200 ms	(195 ms)	208 ms	(205 ms)	219 ms	(214 m)	212 mw	(207 wm)	189 s	(184 ms)	17a(γN-O/γring)
			159 vvw	*(150 w)*		*(142 vw)*	*158 vvw*	*(–)*	*159 vw*	*(157 wm)*		*(–)*	δMON
Δ	123	(116)	135 vvw	(–)	135 vwsh	(–)		(132 vwsh)	145 vvw	(130 vw)	133 vvw	(128 vwsh)	Δ(ring scissors)
E	115	(109)	116 w	(110 w)	123 w	(109 w)	128 vwsh	(–)	129 w	(–)	120 vw	(114 vw)	E(ring scissors)
Z	104	(100)	88 w	(80 w)	94 w	(90 w)	100 w	(91 w)	96 w	(92 w)	92 w	(91 w)	Z(i. rotation) or δOMO
			72 w	*(74 w)*	*73 w*	*(74 w)*	*71 w*	*(72 w)*	*73 w*	*(72 w)*	*72 w*	*(73 w)*	δOMO
					61 vwsh				*62 vwsh*		*62 vwsh*		δOMO

Bold face = M–O stretch, italics = M–O bend. *N.B.* -d_8 bands at 556 cm^{-1} (very strong) and 611 cm^{-1} (strong) not included as they arise from -d_0 bands (modes 11′ and 1) above 630 cm^{-1} (see Tables III and IV).

Cu(II) complex. Such a suggestion, however, would require an explanation for the absence of the ligand band (mode 6a) expected at *ca* 330 to 350 cm^{-1}.

The present ligand isotope study indicates that the former explanation is the more suitable {the 326 cm^{-1}(-d_0)/305 cm^{-1}(-d_8) band frequencies in the Cu(II) complex are typical of the ligand mode rather than of a M–O stretch}. An examination of the Fe(III) complexes for both the -d_0 and -d_8 isotopes with their higher M–O stretches at 412 (394 cm^{-1}) and 380 (371 cm^{-1}) shows both ligand modes 6a at 320 (305 cm^{-1}) and B at 355 (340 cm^{-1}), and so adds further support for the assignments of the -d_0 band between 353 and 326 cm^{-1} to mode 6a. Resolution of this assignment problem would require the use of a metal–isotope study, since if the band at 326 to 350 cm^{-1} is a ligand band which is coupled with νM–O, it will show only slight metal–isotope sensitivity (*e.g.*, with no ^{63}Cu/^{65}Cu sensitivity), while if the band is a relatively pure νM–O it should be significantly shifted on metal–isotope labelling.

A metal-sensitive band of weak to medium intensity found between 300 and 294 cm^{-1} in the bipyO$_2$ complexes is assigned to νM–O. Its frequency is such as to exclude it as a ligand mode. (The only ligand mode candidate is the shear, Γ, which is better assigned to the band between 285 and 265 cm^{-1}.) This band was not assigned by Vinciguerra *et al.*[3] and was masked by νM–NCS in the study conducted by Ahuja and Singh.[5]

Of the three M–O stretches expected for D_3 symmetry, two (three in some of the deuterated spectra) are observed. The M–O bends are found below 200 cm^{-1} in pyO.[16–19] This region also contains three of the non-benzenoid vibrations of bipyO$_2$, modes Δ, E and Z,[13] thereby making the assignments difficult. As is observed for the bipy and phen complexes,[14] the metal–ligand bends are found in two regions. The highest is at about 158 cm^{-1}, and is similar in frequency to δMON in metal(II) complexes of pyO.[16–19] Therefore, while it is a δOMO bend, it is likely to have a significant contribution from bending of the N–O bond and so is described in Table V as δMON. Two bands are observed in the second region below 90 cm^{-1}. The two δOMO bands at *ca* 70 cm^{-1} and *ca* 60 cm^{-1} are found at slightly higher frequency than the δOMO bends in metal(II) complexes of pyO[17] as is to be expected from the chelate effect,[20] and these two bands in bipyO$_2$ are therefore described as δOMO. The two δOMOs are metal-insensitive as was observed for the corresponding vibrations in pyO.[17]

Of the four M–O bends expected, only three are observed. This may be attributed to three causes. First, the bends may be accidentally degenerate as is observed for δOMO in M(II)(pyO)$_6$ complexes.[17] Secondly, the fourth δOMO may lie beyond the range investigated. Thirdly, a band found between 100 and 80 cm^{-1} may also be identified as δOMO, but is considered here to be best assigned to the internal rotation, Z.

Finally, a comment needs to be made concerning the Cu(II) complex. The infrared spectrum (Table V) shows no sign of splitting of the M–O fundamentals into the six νM–O and the nine δOMO bends expected for C_2 symmetry. The absence of such splitting in the stretches may possibly be ascribed to the different coupling within the Cu(II) complex, while the richness of the ligand spectrum in the region in which the bends are expected would make the observation of splitting of the two sets of δOMO bands difficult. Clearly the best indication of Jahn–Teller distortion in the bipyO$_2$ complex with Cu(II) lies in the splitting of some of the ligand bands as a result of the perturbation of the localized ligand symmetry.

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