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Infrared and Raman spectra of heterocyclic compounds—IV The infrared studies and normal vibrations of some 1:1 transition metal complexes of 2,2'-bipyridine

J. S. STRUKL^{*} and J. L. WALTER Department of Chemistry and the Radiation Laboratory[†] University of Notre Dame, Notre Dame, Indiana 46556

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Abstract—Compounds of the formula $ML(X)_2$ (M = Mn(II), Co(II), Zn(II), Fe(II), Pt(II) and Pd(II); L = 2,2'-bipyridine, 2,2'-bipyridine- d_8 ; X = Cl, Br) were prepared and their infrared spectra investigated between 4000–40 cm⁻¹. A normal coordinate analysis was performed on the chloro complexes employing a Urey–Bradley force field with resonance parameter and suitable general valence force field terms about the metal site. Force constants and frequency positions indicate very strong metal–ligand bonding for Pt(II), Pd(II) and Fe(II) and much weaker bonding for Mn(II), Co(II) and Zn(II).

1. INTRODUCTION

CHELATES of 2,2'-bipyridine possess unusual stability in many cases because of the back-bonding potential of the α -dimine chromophore with metals. This is demonstrated among the transition metals where ultraviolet and visible spectroscopy [1-5], magnetic susceptibilities [6], and stability constants and heats of formation [7-9] indicate an anomalously large stability for Fe(II).

In the area of infrared spectroscopy, measurement of the shift in the NH_2 symmetric deformation and the C=N stretching in compounds of the formula



[1, 10] indicate a greater degree of bonding in the Fe(II) chelates than for the other transition metal chelates. For 3:1 chelates of transition metals with 2,2'-bipyridine

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and 1,10-orthophenanthroline, the Fe—N stretching frequencies were observed at 423 and 530 cm⁻¹ vs. 264–297 and 288–300 cm⁻¹ for the other transition metals [7].

Only one normal coordinate analysis has been attempted on a compound similar to 2,2'-bipyridine. Nakamoto found that in



the Fe—N stretching force constant was larger than that for Pt—C in Pt(CN)₄⁻² (4.7 × 10⁵ dyn/cm vs. 3.43×10^5 dyn/cm) [11]. This paper is an attempt to extend these areas by performing an NCA of 1:1 2,2'-bipyridine divalent transition metal chloride chelates. The metals chosen were Pt(II), Pd(II) and Fe(II) with expected strong bonding and Zn(II), Mn(II) and Co(II) with weak expected bonding. The 1:1 chelates were chosen over the more common 3:1 chelates because of their smaller size and computer availability and because of their simpler spectral structure.

The assignments of the chelates are made by comparing the ligand portion to the previously calculated ligand [12] and by a comparison of the deuterated and nondeuterated Pt(II) and Pd(II) chelates. Vibrations about the coordination site are assigned by substitution of the chloride ligand by bromide as well as by comparison to similar halogen and imine chelates.

2. EXPERIMENTAL

2.1 Spectra

The chelates were run as KBr discs [13] and nujol mulls in the 4000–300 cm⁻¹ region on Perkin–Elmer model 221 (NaCl optics from 4000–600 cm⁻¹, CsBr optics from 700–300 cm⁻¹) and 521 spectrophotometers. In the 400–40 cm⁻¹ region, the chelates were run as polyethylene discs [12] on a RIIC Fourier Far IR Spectrophotometer.

2.2 Chelate preparation

 $Pt(2,2'-bipyridine)Cl_2$, $Pd(2,2'-bipyridine)Cl_2$, $Zn(2,2'-bipyridine)Cl_2$ and $Zn(2,2'-bipyridine)Br_2$ were made by adding stoichiometric amounts of ligand and appropriate metal halide (K_2PdCl_4 , K_2PtCl_4 , $ZnCl_2$ and $ZnBr_2$) in ethanol with heating until a precipitate formed [14, 15]. They were washed with water and ethanol and dried *in vacuo* and analyzed for halogen. $Pt(2,2'-bipyridine)Br_2$, $Pd(2,2'-bipy-ridine)Br_2$ were prepared by treating K_2PtCl_4 and K_2PdCl_4 with an excess of KBr before adding a stoichiometric amount of ligand and heating until a precipitate formed. Their halogen content was also analyzed.

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	% Halogen calc.	% Halogen found
Pt(2,2'-bipyridine)Cl ₂	16.80	16.60
Pt(2,2'-bipyridine)Br,	33.90	33.82
Pd(2,2'-bipyridine)Cl.	21.29	21.11
Pd(2,2'-bipyridine)Br.	37.91	37.22
Zn(2,2'-bipyridine)Cl.	24.05	23.92
Zn(2,2'-bipyridine)Br2	41.99	41.95

Analysis:

The remaining chelates were made by decomposition of the 3:1 chelates [6, 16, 17]. To FeCl, dissolved in water and pretreated with iron metal and HCl an ethanol solution of bipyridine (three to one mole ratio) was added. The dark red solution was partially evaporated and the chelate formed on cooling. The 3:1 chelate was then heated in vacuo until a weight loss corresponding to two ligands was obtained as well as yielding the correct halogen content. The bromide salt of the three to one chelate was made by treating the chloride chelate with an excess of KBr. This was then followed by a similar thermal decomposition in vacuo. The cobalt (II) 3:1 chelate was made by stoichiometric addition of anhydrous CoCl₂ and ligand. The bromide was made by treating this solution with excess KBr. The precipitated bromide and chloride 3:1 chelates were then thermally decomposed in vacuum at a temperature of 290°C to assure the formation of the β -isomer. The three to one Mn(II) chelate was made by treating MnCO₃ with HCl followed by a stoichiometric amount of 2,2'-bipyridine. The bromide was made by treating $MnCO_3 \cdot 4H_2O$ with a stoichiometric amount of ligand and then adding KBr until a precipitate formed. These 3:1 chelates were then heated in vacuo at a temperature suitable to yield a loss of two ligands.

Pt(2,2'-bipyridine- $d_8)Cl_2$ and Pd(2,2'-bipyridine- $d_8)Cl_2$ were prepared by stoichiometric addition of deuterated ligand [12] and K_2PtCl_4 or K_2PdCl_4 to D_2O in a sealed container with heating and shaking until a yellow precipitate formed. The precipitate was washed with D_2O and dried *in vacuo*. There was complete loss of the C—H stretching modes between 3000-3100 cm⁻¹.

The hydrochloride was prepared by adding a stoichiometric amount of 1 N HCl to a water suspension of 2,2'-bipyridine and evaporation of the solution *in vacuo* until a precipitate formed.

3. SPECTRAL ASSIGNMENT

The 1:1 metal chelates consist of a ligand portion for which the observed frequencies are found to be comparable to the previously assigned free ligand [12]. These appear in the $4000-400 \text{ cm}^{-1}$ region. The elucidation of hydrogen dependent and non-dependent modes is made by a comparison of the spectra of the Pd(II) and

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.00 cm ⁻¹)	12 L:FeCl	3105 w	-	3075 w†	•	† 3050 w†	* 0000			1600 m	1560 w	1555 w	m 1490 w		1460 s	3 1448 vs	1425 sh		÷		1 1308 m	7 1265 W		1245 m		1 1165 w	1153 m
(4000-4	L:CoC	3110 w	0006	3075 w	3070 w	3065 w	w nene			1590 s 1570 w	1560 m		1488 w		1468 m	1435 ve	1415 w		1420 w		$1310 \mathrm{m}$	1270 W		1245 m		1164 m	1154 m
omplexes	L: MnCl2	3105 w	9006	3070 w		3045 w 9095	M 0700		1559 sh	1590 s 1570 w	1559 m	1558 w	1485 mn		1470 m	1433 vs	1429 w		1410 w		1310 m	1270 w		1240 m		$1162 \mathrm{m}$	1150 m
yridine o	L:ZnCl ₂	3110 m			3078 m	3065 m	III I COC		1601 sh	1592 vs 1570 w	1562 m		1488 s		1469 s	1440 vs	1420 w				1313 s	1264 w		1250 m		1170 w	1166 m
al-2,2'-bip	LD:PtCl ₂	2280 m 2280 m	2280 m	2280 m	2280 m	2280 m	III 0077			1580 mw	1530 m		1435 w		1435 w	1340 vs	1380 w	1365 vw	1310 w		1260 w	1200 w		1240 m			
and met	L: PtCl ₃	3118 w 3110 w	3090 w	3075 w	3052 w	3020 w	M 0100			1598 m 1570 w†	1552 mw		1490 w	1483 vw	1460 s	1440 vs	1428 w		14128	1320 w	1310 m	1268 w	1245 sh	1240 m	1208 w	1170 w†	1166 m
ipyridine	LD: PdCl2	2280 m 2280 m	2280 m	2280 m	$2280 \mathrm{m}$	2280 m	111 0077			1665 m	1530 m		1440 sh		1430 m	1340 vs	1388 m	1350 w	1315 W		1270 w	1208 w		1240 a	1150 w		
for 2,2'-b	L: PdCl ₂	3118 m 3110 w	3090 m 3085 m	3078 m	3057 w	3052 w 2016 w	2100			1595 s	1560 m		1490 m		1460 s	1440 s	1420 wm		1415 W	1317 m	1308 s	1280 w	1245 sh	1240 m	$1205 \mathrm{m}$	1170 w†	1160 s
gnments	L·HCI	3330 w	3080 m			3030 m 3010 m	2790 w 2570 br	1600 s	0001	1600 8	1578 m	1530 vw	1500 s	1470 w	1452 w	I432 s			1410 wm 1390 m	1315 vw	1305 w	1270 s		1230 s		1172 m	1165 sh 1152 vw
and assi	rD*		2295 w 9980 w	2270 w	2255 w						1559 m		1530 m			1345 s			1300.8					1250 ma			
es (cm ⁻¹)	г,		3086 w 3071 w	3064 w	3054 w						1579 s		1553 m			1448 s			8 0141			1270 w		1240 ms		1210 w	
Table 1. Infrared frequenci	Assignment	N—H ⁺ str. C—H(D) str. C—H(D) str.	CH(D) str. CH(D) str.	$C \rightarrow H(D)$ str.	CH(D) str.	C	$N = H^{-1}$ str. $N = H^{-1}$ str. $N = H^{-1}$ str.	N-H+ in pl. bend		ring str. $(U=U U=N)$ 766-770(vs) + 800(w) = 1566-1570	ring str.	$2 \times (766-780) = 1532-1560$	ring str.	760 + 718 = 1478	ring str.	ring str. $+ H(D)$ bend	ring str. $+$ H(D) bend	580 + 770 = 1350	n(D) pend + ring str. N—H ⁺ out of pl. bend	$2 \times \sim 660 = \hat{1}320$	ring str. $+ H(D)$ bend	ring + inter-ring str.		res. dep. ring str.	ring str. $+$ H(D) bend	Hin pl. bend	H in pi. bend

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H in pl. bend H in pl. bend	1138 m		1105 w 1109 w	1120 m 1105 m		1120 w 1105 w		1100 m 1080 wm	1110 w 1105 w	1105 w	1115 w 1100 w
H in pl. bend H in pl. bend	1090 m 1083 m										
ring str. + bend H in pl. bend	1063 m	1033 m	1070 m	1069 m 1060 w 1041 m*	1015 ms	1068 w 1055 w	1017 mw	1070 m 1042 vw	1060 ms 1038 w	1065 w 1040 w	1065 w 1038 w
H out of pl. bend	1039 m			1032 m		1038 w		1025 ms	1038 w	1040 w	1038 w
ring breathing mode	991 m	910 m	1010 w 1005 w	1020 m	890 m	1018 w	992 m	1015 m	1012 m	1015 m	1015 w
ring str. $+$ H bend			980 w	980 w		970 w		972 w	970 w	970 w	
ring str. + H bend				975 w		960 w		965 w	960 w	965 w	
D in pl. bend		965 m			950 mw		960 mw				
H out of pl. bend	890 m		875 w	880 mw		880 w		890 m	906 w	900 w	
D out of pl. bend		827 mw			840 m		848 m				
D in pl. bend		800 W			800 W		M 018				
D in pl. bend		841 w			780 W		A 00/				
D in pl. bend		801 w			770 wm		720 w				
D in pl. bend							710 w				ļ
A_1 ring str. + bend				800 w	745 w	792 w	745 wm		800 w	800 w	8478
D out of pl. bend		734 m			715 mw		692 mw				
H(D) out of pl. bend	753 vs	602 m	760 VB	780 vs	588 в	767 VS	605 w	762 vs	770 VB	764 vs	762 vs
(4 adj.)	738 m	580 s	726 m	732 w		735 w	582 w	730 VB	745 w	745 w	745 w
H(D) out of pl. bend			715 m	718 m		$718 \mathrm{m}$			732 s	730 B	735 a
(4 adj.)	710 w	715 w	705 m			710 vw		700 vw	700 vw	700 vw	700 vw
ring bend	651 w	664 w	660 w	662 w	660 w	670 w	675 w	655 m			665 w
ring bend			640 w	650 m		650 w	663 w	. 650 m	645 w	650 w	655 w
ring bend	618 w	630 w	620 w	645 w	630 w	640 w	625 w	630 w	623 w	630 w	645 w
900 908 - 108			***	479 1111							
				MAA 014		001					
$302 \pm 187 = 489$ $243 \pm 194 = 437$						482 VW		435 vw			
inter-ring bend?				448 w		462 w		465 w			442 w
ring torsion	398 m	$351\mathrm{m}$	435 mw	420 w	362 w	411 w	363 w	416 w	416 w	416 w	417 w
* $L = 2.2$ · bipvridine. $LD = 2.2$ ·	-bipvridine-	<i>d</i>									

* L = 2,2'-bipyridine. LD = 2,2'-bipyridine. d_3 . † Frequency was taken from bromo copmlex.

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Pt(II) deuterated and non-deuterated chelates. The chelates also consist of a metal ligand portion involving the X_2MN_2 portion and the chelate ring for which the

observed frequencies appear in the $400-40 \text{ cm}^{-1}$ region and can be elucidated by halogen substitution. The empirical assignments of the observed modes are given in Tables 1 and 2 and representative observed spectra are shown in Fig. 1.

$3500-2000 \text{ cm}^{-1}$

The chelates possess C_{2v} symmetry with eight possible infrared active aromatic C—H stretching modes. All the chelates exhibit a series of bands, 4–8, in the 3000–3100 cm⁻¹ region. Deuteration shifts these bands to the 2250–2300 cm⁻¹ region.

$2000-1300 \text{ cm}^{-1}$

There are four bands between $1600-1460 \text{ cm}^{-1}$ that shift approximately $30-50 \text{ cm}^{-1}$ on deuteration. These absorptions are principally ring stretching vibrations similar to the bands at 1570 and 1553 cm⁻¹ in the free ligand [12]. All the chelates also exhibit a very strong band at 1440 cm⁻¹ similar to the free ligand band at 1448 cm⁻¹. In both cases, deuteration shifts this absorption to 1340 cm⁻¹ and is assigned as a ring mode with significant hydrogen dependence.

The remainder of the region can exhibit anywhere from three to five bands for the various complexes (a series of shoulders on the 1440 cm⁻¹ band and the splitting of a band at 1320 cm⁻¹ in the hydroperchlorate salt and the Pt(II) and Pd(II) chelates). SINHA [18] and TAYLOR [19] reported the appearance of a new band (unsplit) at 1320 cm⁻¹ for 3:1 rare earth and transition metal bipyridine chelates. BELLAMY [20] indicates the presence of two bands in this region separated by approximately 100 cm⁻¹ due to interaction between the C—C and C—N species.

Pd(bipy)Cl₂ and Pt(bipy)Cl₂ display absorptions at 1430, 1415, 1317 and 1308 cm⁻¹. The 1415 and two 1300 cm⁻¹ bands (considered as one) are assigned as the ring stretching modes of Bellamy and possess A_1 symmetry. The 1430 cm⁻¹ band is assigned as a B_1 ring stretching mode with some hydrogen bending character. Deuterations shifts these bands to 1388, 1270 and 1315 cm⁻¹ respectively.

 $1300-1100 \text{ cm}^{-1}$

An absorption appears at approximately 1240 cm^{-1} in all the complexes and is similar in behavior on deuteration to that of a similar band in 2,2'-bipyridine [12]. Partial deuteration does not affect its position and intensity whereas all other hydrogen dependent modes are significantly affected. As in the ligand, it is assigned

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	Table 2.	Infrared	frequenci	es (cm ⁻¹)	and assign	nments for	r metal-2,	2'-bipyrid	line compl	lexes(400-	40 cm ⁻¹)		
******	HCI	PdCl	PdBr,	PtCl_	PtBr ₃	2,2 ZnCl ₃	'-Bipyridine ZnBr ₂	MnCl ₂	MnBr	CoCl ₂	CoBrs	FeCI,	FeBr ₂
M—N str. + MCl + chelate ring str. M—Cl asym. str. M—Cl sym. str.		409 w 365 s 340 s	396 w	386 w 360 vs 357 m	378 w	369 w 339 vs 329 vs	366 w	357 w 259 sh 248 s	361 w	n.o. 338 s 313 m	1.00. 1.00.	423 W 369 vs 361 vs	436 w
M—N str. + bend MN ₉ scis. bend MBr asym. str. MBr sym. str.		280 m 251 m	302 m 294 m 228 vs 196 ms	295 m 261 m	307 w n.o. 228 vvs	243 ms 194 ms	217 ms 192 ms 266 vs 266 vs	239 s 232 sh	235 s 212 ms 212 ms 197 s	200 BIR 270 B 268 ms	256 s 222 m 201 m 180 s	318 s 278 w	288 s 263 w 242 w1 219 vs
chelate ring str.	213 ah 200 vs	206 ms	192 m	210 mw 201 mw	208 w	183 w	114 W	182 w	183 ah	194 w 187 w	192 w	219 mw 213 mw	201 w 186 w
MCl ₃ + MN ₃ sois. bend MBr ₂ + MN ₂	172 vvw	174 W	124 w	174 w	123 w	172 ms	169 ms	174 w	169 m	174 w	150 w	200 mw	168 w
MCl _a bend MBr ₂ bend MBr ₂ bend 2 × 72 = 144 poly.	155 w 136 w	152 w 141 w	118 w 138 w	154 w 140 w	111 w 140 w	136 ms	104 w 140 w	165 w 147 w 141 w	123 w 140 sh	162 w	118 w	147 m	118 w 144 ah
MCI _s bend MBr _s bend		136 w				120 w		120 w	117 w 111 w	147 w	112 w	122 w	106 w
Torsion inter-ring mode? erystal} modes }	96 ms 110 w 48 vw	92 w 67 w 64 w	81 w 108 w 49 w	114 w 60 w 60 w	86 w 69 vw 48 vw	02 sh	95 sh	93 m 87 w 62 w 54 w	87 w 54 w	95 w		81 w	84 W

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Fig. 1

to the resonant dependent ring stretching mode. There are also two weak intensity bands at $1269-1280 \text{ cm}^{-1}$ and $1200-1210 \text{ cm}^{-1}$ in all the chelates which produce weak bands appearing at $1208 \text{ and } 1150 \text{ cm}^{-1}$ in the deutero chelates. These bands are assigned as ring stretching vibrations.

There are four remaining bands in this region appearing at $1150-1170 \text{ cm}^{-1}$ (two) and $1100-1120 \text{ cm}^{-1}$ (two). These bands shift upon deuteration to 980, 865 and $\sim 800 \text{ cm}^{-1}$ and correspond to the free ligand hydrogen dependent modes at 1210 and 1138 cm⁻¹.

$1100-800 \text{ cm}^{-1}$

This region exhibits the remaining in-plane hydrogen bending motions at ~ 1058 and 1041 cm^{-1} (shift to 700-776 cm⁻¹ upon deuteration). A ring stretching and bending motion is found at 1064 cm⁻¹ (shifts 54 cm⁻¹ to 1015) and is similar to the



Fig. 1 (cont.)

1063 cm⁻¹ free ligand band which shifts 30 cm^{-1} on deuteration. The ring breathing motion at 1020 cm⁻¹ is shifted 30 cm^{-1} to higher frequencies in the metal complexes; chelation shows the same trend in pyridine complexes [18]. The initial hydrogen out-of-plane modes at 1039 and 880 cm⁻¹ shift to 848 and 692 cm⁻¹ on deuteration. A new band at approximately 800 cm⁻¹ appears that corresponds to an infrared inactive ring mode of the free ligand.

800-600 cm⁻¹

The characteristic aromatic out-of-plane substitution dependent hydrogen modes and the ring bending motions occur in this region. All the complexes possess four adjacent hydrogen atoms and display a very intense absorption at 770–760 cm⁻¹ and a medium intensity absorption at 730–740 cm⁻¹. Most of the complexes also have a weak absorption sandwiched between these two. Deuteration shifts these bands to



Fig. 1 (cont.)

602(m) and 560(s) cm⁻¹ exhibiting the same apparent reversal in intensity as those in the free ligand [12].

The ring bending motions are three in number and appear between 670 and 625 cm⁻¹ for all the complexes. GALL noted that in Mpy_2X_2 complexes [21] these absorptions were metal dependent (Pt = Pd > Cu > Ni > Co > Mn). The same might be said here for the lowest frequency mode which produces the order: Fe(645), Pd(645), Pt(640), Co(630), Zn(630) and Mn(623).

 $600-400 \text{ cm}^{-1}$

DURIG [22] originally reported the Pd---N stretching frequency of a large series of

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N-imine complexes (pyridine, 1,10-orthophenanthroline, 2,2'-bipyridine, etc.) as appearing in the 450-500 cm⁻¹ region. This, however, does not appear to be reasonable since one would not expect metal-pyridine stretching frequencies to appear as high as 2,2'-bipyridine or 1,10-orthophenanthroline M—N stretches. Also, two bands of weak intensity are observed in this region for the HCl salt of 2,2'bipyridine as well as for the Pd(II), Pt(II), Zn(II) and Fe(II) chelates under normal conditions and for Mn(II) and Co(II) under $5 \times$ ordinate expansion. Instead, the bands in this region are possibly overtone or combination bands of the metal-nitrogen dependent modes in the 200-300 cm⁻¹ region. Also, the calculations predict an inter-ring type mode (in plane shearing: biphenyl, 302 cm⁻¹; bipyridine, 319 and 482 cm⁻¹ calculated) occurring above 400 cm⁻¹. Very tentatively, the lower of these bands is assigned as the inter-ring type mode.

Similar to the free ligand, a torsional ring motion appears at $\sim 420 \text{ cm}^{-1}$. This is about 20 cm⁻¹ higher than in the free ligand but the same trend is observed in pyridine complexes. Deuteration shifts it to 362 cm⁻¹ (351 cm⁻¹ for the free ligand).

Below 400 cm⁻¹

The general characteristics of the spectra in this region are: (a) a weak band above 350 cm^{-1} (shift slightly on bromination), (b) two bands between $300-350 \text{ cm}^{-1}$ (shift significantly on bromination), (c) two bands between $220-300 \text{ cm}^{-1}$ (shift slightly on bromination), (d) two bands spaced $20-30 \text{ cm}^{-1}$ apart between $160-210 \text{ cm}^{-1}$, and (e) a series of bands below 160 cm^{-1} .

The absorptions between 300 and 350 cm⁻¹ (259 and 248 for the Mn(II) complex) are assigned as the metal-chlorine stretching vibrations because of their: (a)



Fig. 1. Infrared absorption spectra of 1:1 metal-bipyridine halide complexes. (A) $Pd(dipy)Cl_2$; (B) $Pt(dipy)Cl_2$; (C) $Pd(dipy-d_8)Cl_2$; (D) $Pt(dipy-d_8)Cl_2$; (E) — $Pd(dipy)Cl_2$, \cdots $Pd(dipy)Br_2$; (F) $Dipy-HCl 3300-700 \text{ cm}^{-1}$; (G) $Zn(dipy)Cl_2$; (H) $Mn(dipy)Cl_2$; (I) $Co(dipy)Cl_2$; (J) $Fe(dipy)Cl_2$; (K) $Dipy-HCl 700-40 \text{ cm}^{-1}$; (L) — $Zn(dipy)Cl_2$, \cdots $Zn(dipy)Br_2$; (M) — $Mn(dipy)Cl_2$, \cdots $Mn(dipy)Br_2$; (N) — $Co(dipy)Cl_2$, \cdots $Co(dipy)Br_2$; (O) — $Fe(dipy)Cl_2$, \cdots $Fe(dipy)Br_2$; (P) $Pd(dipy)Cl_2$; (Q) $Pd(dipy)Br_2$; (R) $Pt(dipy)Cl_2$; (S) — $Pt(dipy)Br_2$, \cdots $Pt(dipy)I_2$; (T) $Zn(dipy)Cl_2$; (U) $Zn(dipy)Br_2$; (V) $Mn(dipy)Cl_2$; (W) $Mn(dipy)Br_2$; (X) $Co(dipy)Cl_2$; (Y) $Co(dipy)Br_2$; (Z) $Fe(dipy)-Cl_2$; (Z2) $Fe(dipy)Br_2$; (P) = polyethylene; (M) = mylar band; (S) = spurious band.

Compound	M—X str.	Reference	M(dipy)X ₂ M-X str.
Pdpy _o Cl _o	342, 333	[23, 24]	335, 340
Pdpy Br.	219, 210	[24]	228, 196
Ptpy,Cl.	343, 327	[25]	250, 337
Ptpy _s Br _s	218, 209	[23]	228, 206
PtCl,-2	335, 304	[26-28, 30]	
Znpy.Cl.	329, 293	[23, 29]	339, 324
Znpy ₃ Br ₂	254, 220	[23, 29]	256, 250
$Copy_2Cl_2$	344, 304	[23]	338, 313

Table 3. Metal-halogen stretching frequencies

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generally strong intensity, (b) shift to significantly lower frequencies on bromination and (c) similarity to other metal halogen compounds as shown in Table 3.

The weak absorption above 350 cm^{-1} and the two medium intensity bands between $220-300 \text{ cm}^{-1}$ are assigned as metal-nitrogen dependent modes. The latter bands shift to higher frequencies in the platinum and palladium complexes and to lower frequencies for the others while remaining in the same region on halogen substitution. The high frequency band appears near the 420 cm^{-1} ligand out-of-plane mode for Fe(II) and Pd(II) and might be interpretable as splitting of, or related to, the 420 cm^{-1} absorption. This does not appear to be the case since: (a) only the 420 cm^{-1} band shifts on deuteration while the other band remains fixed, (b) this band shifts slightly on halogen substitution whereas the 420 cm^{-1} band remains fixed, (c) the bands above 350 cm^{-1} vary in a logical order among the metals from Mn(357) to Fe(423), and (d) three-to-one chelates show only Fe(II) having a band close to the 420 cm^{-1} band.

In the case of $Pt(dipy)Br_2$, the two low frequency bands were not observed by the interferometer although a weak band appeared at 307 cm⁻¹ in the CsBr region. WALTON [31] did not note any bands in this region either but DURIG [24] reported

Compound	MX ₂ def	Reference
PtCl4-2	184 (R), 168–175 (IR)	[26, 32]
$PtBr_4^{-2}$	135 (R),	[26, 32]
Ptpy ₂ Cl ₂	163 (IR)	[24]
Pdpy ₂ Cl ₂	166 (IR)	[24]
cis-Pt(NH ₈) ₂ Cl ₂	198 (IR)	[30]
Znpy ₂ Cl ₂	200 (IR)	[33]
Znpy ₂ Br ₂	182 (IR)	[33]

Table 4. Representative MX₂ bending deformations

observing bands of weak intensity at 301 cm^{-1} and 289 cm^{-1} which would correspond well to the 307 cm^{-1} band and the two bands in the chloro complex.

The next set of bands is two in number between $210-170 \text{ cm}^{-1}$. The higher frequency band shifts only a few wavenumbers on halogen substitution while the lower frequency band shifts $30-50 \text{ cm}^{-1}$. Bending motions of the MX₂ species have been reported in this region for some divalent Pd, Pt and Zn complexes as shown in Table 4. Consequently, the lower band with its greater shift, is assigned as principally an MX₂ scissors type deformation occurring at $126-140 \text{ cm}^{-1}$ in the bromo complexes. The higher frequency band, because of its slight shift, is assigned as a chelate ring type mode similar in character to the free ligand mode at 169 cm^{-1} .

Assignment of the remaining bands is somewhat difficult because of their number, randomness and weak intensities. The remaining MX_2 bending vibrations are assigned in this region (wagging, twisting, etc.). There is a band in all of the complexes at approximately 90–100 cm⁻¹. This may be a chelate ring motion with character similar to that of the free ligand modes at 42 or 92 cm⁻¹ [12]. These tentative assignments can be seen in Tables 1 and 2.

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-	Pd (by	/pr)Cl ₂		Pd(bypr-	d ₈)Cl ₈
Frequency	obs.	calc.	Approximate description	obs.	cale
A_1 modes					
1	3110	3078	C-H(D) str.	2280	2279
2	3085	3074	C-H(D) str.	2280	2268
3	3057	3072	C-H(D) str.	2280	226
4	3015	3070	C-H(D) str.	2280	225
5	1595	1584	C-C, C-N, C-C _{ir} str.	1565	1576
6	1460	1493	CC, CN str.	1430	1473
7	1430	1448	CC, CC _{i.r.} str.	1388	1417
8	1317	1353	C-C, C-N str., H(D)CN def.	1270	1279
9	1245	1263	resonance depdt. ring str.	1240	1228
10	1208	1226	C-C, C-N str., CCH(D) def.	1150	1150
11	1160	1155	CN str., CCH(D) def.	868	91
12	1105	1098	CCH(D) def.	800	813
13	1041	1043	CCH(D) def., C-C str.	780	780
14	980	1014	CCH(D) def., C-C str.	770	776
15	1069	1062	C-C, C-N, M-N str.	1015	1037
16	800	785	CCN, CNC def.	745	73(
17	650	676	CCN, CCC def.	630	648
18	409	400	MN, CC _{i.r.} , CN _{i.c.r.} str.	378	38
19	340	344	MCl str. (sym.)	330	342
20	251	249	MN ₂ seis. def.		239
21	206	202	MN ₂ - MX ₂ scis. def.		193
22	174	174	$MN_2 + MX_2$ sois. def.		16
B ₁ modes					
23	3118	3078	CH(D) str.	2280	2272
24	3090	3073	C-H(D) str.	2280	226
25	3078	3072	C-H(D) str.	2280	226
26	3032	3070	C - H(D) str.	2280	225
27	1560	1556	C-N. C-C str.	1530	154
28	1490	1523	C-C. C-N str.	1440	150
29	1440	1403	C-C str., CCH(D) def.	1340	135
30	1415	1381	C-C, str., CCH(D) def.	1315	131
31	1280	1281	C-C, C-N str., CCH(D) def.	1208	123
32	1170	1178	CCH(D) def.	950	94
33	1120	1099	CCH(D) def.	800	78
34	1060	1059	CCH(D) def.	780	770
35	1032	1045	CC str., CCC, CCH(D) def.	990	100
36	1020	1020	ring breathing	990	99
37	975	996	CCC, CCH(D) def., CC str.	770	760
38	662	675	CCC def., MN str.	660	65
39	645	646	CCC, CCN def.	630	628
40	448	458	inter-ring def.	n.o.	428
41	355	350	MX. asym. str.	340	348
42	280	274	MN + MX str.		264
43	57	60	MX ₂ wag	—	51
B ₂ modes					
44	1032	1037	Π —H wag	840	813
45	880	890	II-H wag	714	759
46	758	766	П H wag	588	611
			č	605	639
47	732	738	Π —H wag	588	534
48	718	703	Π —H wag, ring τ		
49	420	426	ring τ	372	388
50	n.o.	242	ring τ)	
51	152	152	MCl _a wag	1 mot	
52		74		106 run	
53		22			

Table 5. Observed and calculated frequencies of $Pd(2,2'-bipyridine)Cl_2$ and $Pd(2,2'-bipyridine-d_8)Cl_2$

i.r.: inter-ring. i.c.r.: in chelate ring.

n.o.: not observed.

Bond stretch	(K)	Angle bend (H) and repuls	ion (F)	Resonance	ρ
MX	1.708	XMX	0.13	0.13	nyd ring	0.35
MN	2.64	NMN	0.109	0.196	chelate ring	0.25
CN	4.15	NMX	0.039	0.072	B	
CC _{i.r.}	4.00	CNM _{1.C.T.}	0.066	0.112		
CC	5.06	CNM	0.16	0.46		
СН	4.70	CCN	0.32	0.72		
OVF		CCNi.r.	0.20	0.43		
GVI		. CNC	0.19	0.40		
(NM) (MX)	0.135	CCC	0.26	0.92		
(NMN) (XMX) opp.	0.10	CCC _{i.r.}	0.40	0.60		
(XMN) (XMN) opp.	0.10	CCH	0.16	0.39		
(XMN) (XMN) adj.	0.193	NCH	0.18	0.42		
(NMN) (XMN) adj.	0.00					
	· · · · · · · · · · · · · · · · · · ·				·····	
Torsion (7)		out of plane	wag (II)	7	7 interaction force	constants
C-Ni er	0.50	H(22)	0 255		611.611	0
C	0.225	H(20)	0.298		71 E 71 E 17 C) 17 C)	-0.035
cc	0.578	H(18)	0.282		<i>NVINU</i>	0.000
C-N	0.50	$\mathbf{H}(16)$	0.275			
M—N	0.301	()				
			,, , <u>, , _</u>		· · · · · · · · · · · · · · · · · · ·	
ortho Torsion in	ter.	meta I	forsion		ortho π–τ i	nter.
(C-C) (C-N)	0.06	(C-C) (C-C	.) 0.1	0	H(22) (C-N)	0.059
(CC)i.r. (CN)i.c.r	0.09	(C-C) (N-1	1) 0.0	6	H(22) (C-C)	0.02
(C-N) (C-N)	0.10	(C-C) (C-N	0.0	6	H(20) (C-C)	-0.12
(CC) (CC)	0.115	(C-N) (C-1	N) 0.0	5	H(18) (C-C)	0.063
(C—N) (M—N)	0.06	(N-M) (C-1	N) 0.1	D	H(16) (C-C)	-0.10
(N-M)(N-M)	0.31		·			

Table 6. Force constants for Pd(2,2'-bipyridine)Cl₂ in mdyn/Å

i.r.: inter-ring. i.c.r.: in chelate ring.

Table 7. Metal-ligand dependent frequencies and force constants for 2,2'-bipyridine 1:1 metal complexes

Observed frequencies for :	2,2'-bipy	ridine 1:1	metal co	mplexes (c	m ⁻¹)	
	Pt	Pd	Fe	Co	Zn	Mn
A_1 sym. $MN + MCl + chelate$ ring str.	385	409	423	371*	369	357
B ₁ asym. MN str.	295	280	318	270	243	239
A ₁ MN ₂ and MCl ₂ and chelate ring type bond	201	206	219	194	183	182

For	rce constan	nts for 2,2'	-bipyridin	e 1:1 meta	l complexe	8	
(mydn/Å)	lig	\mathbf{Pt}	Pd	Fe	Co	Zn	Mn
<i>K</i> (M—N)		2.97	2.64	2.19	0.62	0.54	0.37
K(N-C)	6.10	4.15	4.15	4.15	4.90	5.15	5.35
p(chel.) resonance		0.25	0.25	0.50	0.25	0.25	0.25
p(py. ring)	0.35	0.29	0.29	0.25	0.31	0.32	0.32

* Calc.

4. DISCUSSION

Normal coordinate analyses were performed for all the complexes studied, using the Wilson's **GF** matrix method. The complexes possess either square planar or tetrahedral configurations and C_{2v} symmetry with 43 in-plane and 10 out-of-plane infrared active fundamentals. Since no X-ray crystal data was available for the complexes, a set of molecular parameters had to be generated. The angles and bonds in the ligand portion of the chelates were those employed for the free ligand [12] and the chelate ring angles were chosen so as to yield the M—N bond lengths of 2.0 Å for Pd and Pt and 1.90 Å for the remaining transition metals. These parameters seemed reasonable for the approximate calculations presented here and give a set of force constants, which although perhaps not unique, give a good insight into the type of metal bonding that are possessed by these complexes.

A sample calculation is given in Table 5 for $Pd(dipy)Cl_2$ with an approximate description derived from the potential energy distributions of the symmetry coordinates. The force constants used to generate these frequencies are given in Table 6.

The pertinent frequencies and force constants for the 1:1 chelates are given in Table 7. In general, Pd, Pt and Fe form much stronger complexes than Mn, Co and Zn indicating that substantial back-bonding occurs in the former but not in the latter group of divalent metal complexes.

This is reflected in the M—N dependent frequencies which among themselves form two groups consisting of Pt, Pd and Fe at higher frequencies than Mn, Co and Zn. Since there are no pure M—N stretching frequencies in these chelates, one might be presumptive to compare them to other molecules. It might be noted that the B₁ mode around 230–300 cm⁻¹ contains a high degree of asymmetric stretching character and it falls between ν (M—N) found for pyridine and ammonia complexes [23, 25, 27, 30, 34–36]. This is reasonable since ammonia is a stronger base and smaller molecule and pyridine, even though being a stronger base, lacks the chelation effects.

The force constants reflect the bonding trend to a much greater degree than the frequencies. Divalent Pd, Pt and Fe have K(MN) force constants four times as large as the other metals indicating that there is considerable back-bonding involved in the former group. The (Fe—N) force constant is not as large as that observed by Nakamoto in Fe(GMI)₃⁺² (4.55 mdyn/Å [11]). This is not unreasonable since the GMI complex involves three ligands with greater extent of back bonding than the 1:1 bipyridine chelates reported here. The bonding trend is also reflected in the K(CN) and resonance force constants which are lower for Pd, Pt and Fe complexes than for Mn, Zn and Co complexes. In comparing the K(MN) force constant to those for imidazole and benzimidazole [33] one sees that the Mn, Co and Zn chelates involve only a normal chelate bond since their force constants are very much similar to the imidazole and benzimidazole complexes.

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