Based on the results obtained above, we have assigned the infrared and Raman spectra of *trans*-Pd(PPh_3)$_2$$X_2$ and *trans*-Pd($AsPh_3$)$_2$$X_2$ (X = Cl and Br) containing the metal of natural abundance. Table III lists the observed frequencies and band assignments. Previously, Park and Hendra[6] assigned the M–X and M–P stretching vibrations of analogous trimethylphosphine and trimethylarsine complexes. Our M–X frequencies shown in Table III are very close to those reported by Park and Hendra.[6,15] However, our Pd–PPh_3 (190–150 cm^{-1}) and Pd–$AsPh_3$ (180–130 cm^{-1}) stretching frequencies are markedly lower than their Pd–PMe_3 (360–340 cm^{-1}) and Pd–$AsMe_3$ (280–260 cm^{-1}) stretching frequencies, respectively.

Approximate Normal Coordinate Analysis. In the previous sections, we have assigned the M–P and M–X stretching bands based on the observed isotopic shifts. It is, therefore, desirable to compare them with theoretical isotopic shifts calculated from normal coordinate analysis. Since the $M(PEt_3)_2X_2$-type molecule is too complex to carry out a rigorous treatment, we have adopted a *trans* planar MY_2X_2 model assuming that the PEt_3 ligand is a single atom having the mass of PEt_3. Evidently, such an approximate calculation provides only a rough measure of theoretical isotopic shifts. Even so, the results are sufficient to show that the magnitudes of the observed isotopic shifts are at least reasonable.

Table IV compares the theoretical and observed isotopic shifts of *trans*-Pd(PEt_3)$_2$$X_2$ (X = Cl and Br) due to ^{58}Ni–^{62}Ni substitution. The molecular parameters used were: Ni–Cl, 2.30; Ni–Br, 2.40; Ni–P, 2.25 Å.[16] The four angles around the Ni atoms were assumed to be 90°. The potential energy was expressed by using the Urey–Bradley field.[17] The following set of force constants was found to be satisfactory: *K* (stretching), 1.35 for Ni–Cl, 1.25 for Ni–Br, and 0.75 for Ni–P; *H* (bending), 0.11; *F* (repulsive), 0.13 (all in units of mdyn/Å). The results shown in Table IV indicate that (1) the magnitude of the observed isotopic shifts is close to that expected theoretically and (2) the isotopic shifts for bending modes are less than 2 cm^{-1} in these cases.

Table IV. Comparison of Theoretical and Observed Isotopic Shifts for *trans*-Ni(PEt_3)$_2$$X_2$ (cm^{-1})

	Theoretical		Observed	
	^{58}Ni	$\Delta\bar{\nu}$	^{58}Ni	$\Delta\bar{\nu}$
	$Ni(PEt_3)_2Cl_2$			
Ni–Cl stretch	402.4	7.2	403.3	6.7
Ni–P stretch	270.8	7.3	273.4	5.9
Ni–Cl bend	189.5	0.0	186.5	−0.2
Ni–P bend	168.2	1.7	161.5	−0.5
	$Ni(PEt_3)_2Br_2$			
Ni–Br stretch	340.9	8.6	337.8	10.5[a]
Ni–P stretch	265.9	7.5	265.0	4.7
Ni–Br bend	141.0	0.1	155.1	1.5
Ni–P bend	147.1	0.5	*b*	

[a] See footnote *a* of Table I. [b] Hidden by the neighboring band.

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(15) In ref 6, there seem to be obvious errors in designation of vibrational modes: In Table II, ν_1 and ν_2 represent the M–P or M–As stretching, whereas ν_3 and ν_4 denote the M–halogen stretching modes.

(16) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, Special Publication No. 11, 1958, and Special Publication No. 18, 1965.

(17) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

Metal Isotope Effect on Metal–Ligand Vibrations. II. Tris Complexes of 2,2′-Bipyridine and 1,10-Phenanthroline[1,2]

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Abstract: The far-infrared spectra (500–150 cm^{-1}) of the isotopic pairs have been obtained for the $[Fe(bipy)_3]^{2+}$ (^{54}Fe and ^{57}Fe), $[Ni(bipy)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ (^{58}Ni and ^{62}Ni), and $[Zn(bipy)_3]^{2+}$ and $[Zn(phen)_3]^{2+}$ (^{64}Zn and ^{68}Zn) ions. Based on the observed isotopic shifts, the Fe–N, Ni–N, and Zn–N stretching bands have been assigned at 375–360, 300–240, and 240–175 cm^{-1}, respectively.

The infrared spectra of tris complexes of 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) with the first-row transition metals have been studied by several investigators. Schilt and Taylor[3] and Inskeep[4] studied the infrared spectra of these compounds in the regions from 2000 to 600 and 2000 to 250 cm^{-1}, respectively, and Clark and Williams[5] extended the infrared measurements down to 60 cm^{-1}. As noted by these investigators, the bands observed in the high-frequency region are mainly due to the ligand vibrations slightly perturbed by coordination and cannot be correlated to the nature of the metal. On the other hand, the spectra below 500 cm^{-1} are different for each metal involved. Attempts have been made to assign the metal–nitrogen (M–N) stretching vibrations in this region. Inskeep[4]

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(2) Supported by a Petroleum Research Fund unrestricted research grant (3318-C3,5), administered by the American Chemical Society, and a U. S. Army Research Grant (DA-ARO-D-31-124-G1130).

(3) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

(4) R. G. Inskeep, *ibid.*, **24**, 763 (1962).

(5) R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **23A**, 1055 (1967).

Table I. Observed Frequencies, Isotopic Shifts, and Band Assignments for $[Fe(bipy)_3]^{2+}$ Ion (cm^{-1})

bipy[a]	$[Fe(bipy)_3)]Cl_2 \cdot 5H_2O$		$[Fe(bipy)_3]$-$I_2 \cdot xH_2O$[a]	$[Fe(bipy)_3]$-$(BF_4)_2 \cdot xH_2O$[a]	$[Fe(bipy)_3](ClO_4)_2$[a]			Assignment[h]
					Fe	^{54}Fe	$\Delta\bar{\nu}$[d]	
423	423[b]	419[c] (w)	423 (s)	425 (s)	418 (s)[e]	418.5	0.1	Ligand (A)
404								
			385 (w)	386 (w)	381 (m)	386.0	*6.0*	ν (Fe–N)
	364[b]	~374[c] (vw)	380 (sh)	380 (sh)	374 (m)	376.2	*5.2*	
			364 (m)	365 (m)	*g*	*g*		Ligand (B)
				278 (vw)	283 (vw)	*f*		Ligand (C)
					237 (w)	238.2	−0.6	Ligand (D)
			211 (m)	211 (m)	203 (w)	*f*		δ (N–Fe–N)
								Ligand (E)
				193 (w)	190 (w)	190.0	0.0	
			183 (w)	183 (w)				Ligand (F)
168			173 (vw)	161 (vw)	163 (vw)	*f*		

[a] Present work. [b] Reference 4. [c] Reference 5. [d] $\Delta\bar{\nu}$ indicates an isotopic shift, $\bar{\nu}(^{54}Fe) - \bar{\nu}(^{57}Fe)$. [e] The perchlorate shows bands at *ca.* 497 and 476 cm^{-1} which show no shifts by isotopic substitution. [f] Too weak to be observed with a milligram scale sample. [g] Hidden by the neighboring band. [h] ν, stretching; δ, bending.

assigned the M–N stretching vibrations of tris(bipy) complexes with Co(II), Ni(II), Cu(II), and Zn(II) in the region from 300 to 260 cm^{-1}. In making these assignments, he assumed that the highest frequency band which is absent in the free ligand is the M–N stretching vibration. Clark and Williams,[5] on the other hand, assigned the bands at 280–230 cm^{-1} of the Ni(II) and Co(II) complexes to ligand vibrations newly activated by complex formation and concluded that no bands above 200 cm^{-1} can be assigned to the M–N stretching vibrations.

As stated above, the M–N stretching vibrations of tris(bipy) complexes have been extremely difficult to assign on an empirical basis. Furthermore, the structures of these compounds are too complicated to allow rigorous vibrational analysis. Recently, we have developed the metal isotope technique[6] to assign metal-ligand vibrations of coordination compounds. In this paper, this technique has been applied to the tris(bipy) and tris(phen) complexes of Fe(II), Ni(II), and Zn(II).

Experimental Section

All the compounds were prepared by literature methods.[3,4,7,8] Metal complexes containing pure metal isotopes were prepared on a milligram scale. All the metal isotopes were purchased from Oak Ridge National Laboratory. The purity of each metal isotope was: ^{58}Ni (99.98%), ^{62}Ni (99.02%), ^{54}Fe (98.19%), ^{57}Fe (90.73%), ^{64}Zn (99.66%), and ^{68}Zn (98.50%). The Ni isotopes were obtained as the metal, while the Fe and Zn isotopes were received as the oxides. In order to obtain an aqueous metal solution, metallic nickel and zinc oxides were dissolved in 6 *N* HCl and converted to the chlorides. Ferric oxide was reduced to metallic iron by passing hydrogen gas over it at 400° for 4 hr. Metallic iron was then dissolved in sulfuric acid to obtain aqueous $FeSO_4$ solution. The ligands, bipy and phen, were purchased from Aldrich Chemical Co., Milwaukee, Wis. The purity of each complex was checked by comparing the spectrum with that of the corresponding complex containing the metal of natural abundance as reported in the literature.

Infrared spectra were measured on a Beckman IR 12 (4000–250 cm^{-1}) and a Hitachi Perkin-Elmer FIS-3 (400–33 cm^{-1}) infrared spectrophotometer. A Nujol mull with polyethylene plates was used to obtain the spectra of solid samples. The spectra were run with a scanning speed from 1 to 2 cm^{-1}/min. Reproducibility of the spectra was checked by running the spectra three to five times. The average error in frequency reading was 0.5 cm^{-1}.

Results and Discussion

$[Fe(bipy)_3]^{2+}$ Ion. The infrared spectrum of $[Fe(bipy)_3]Cl_2 \cdot 5H_2O$ has been measured by Inskeep[4] and Clark and Williams.[5] Both investigators reported only two bands at *ca.* 420 and 365 cm^{-1}. We have measured the spectra of the iodide, tetrafluoroborate, and perchlorate. For the perchlorate, we have prepared a pair of isotopic species containing ^{54}Fe and ^{57}Fe. All the observed frequencies below 500 cm^{-1} are listed in Table I.

The free bipy ligand exhibits the bands at 423–404 (A) and 168 cm^{-1} (F). These bands are expected to appear at approximately the same frequencies in all metal-bipy complexes studied. They are insensitive to metal isotope substitution. Thus, the bands at *ca.* 430–410 and 170–160 cm^{-1} observed for the Fe(II) complexes were assigned to these ligand vibrations. As is shown in Table I, two bands at 386.0 and 376.2 cm^{-1} of $[^{54}Fe(bipy)_3](ClO_4)_2$ are shifted by 6.0 and 5.2 cm^{-1}, respectively, to lower frequencies by the ^{54}Fe–^{57}Fe isotopic substitution. Thus, these bands must be assigned to the Fe–N stretching modes. Previously, Inskeep[4] assigned the band at 423 cm^{-1} of the chloride to the Fe–N stretching mode.

Several bands observed at 375–355 (B), 290–275 (C), 260–235 (D), and 240–210 (E) cm^{-1} have been assigned to ligand vibrations newly activated by complex formation. In fact, these bands appear consistently in tris(bipy) complexes of Ni(II) and Zn(II) although in certain cases they are overlapped by the M–N stretching bands. It should be noted that a band which does not appear in the free ligand is not necessarily due to a metal-ligand vibration since complex formation may activate some ligand vibrations which are inactive in the free state.[5,10]

$[Fe(phen)_3]^{2+}$ Ion. Table II lists the observed frequencies for the three salts studied. The Fe–N stretching frequencies of the $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ ions are expected to be similar, since the structure and bonding of these two complex ions are similar. Thus, the two bands at *ca.* 375 and 360 cm^{-1} which appear consistently in the three salts of the $[Fe(phen)_3]^{2+}$ ion have been assigned to the Fe–N stretching modes.

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(6) K. Nakamoto, K. Shobatake, and B. Hutchinson, *Chem. Commun.*, 1451 (1969).

(7) F. M. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(8) R. Morgan and F. H. Burstall, *ibid.*, 2213 (1931).

Table II. Observed Frequencies and Band Assignments for $[Fe(phen)_3]^{2+}$ Ion (cm^{-1})

phen	$[Fe(phen)_3](BF_4)_2$	$[Fe(phen)_3](ClO_4)_2$	$[Fe(phen)_3](NO_3)_2$	Assignment
432 (w) 411 (s)	438 (w) 429 (w)	438 (w) 428 (w)	430 (vw)	Ligand (A)
	375 (w) 359 (m)	374 (w) 359 (m)	373 (vw) 359 (m)	ν (Fe–N)
	296 (s) 288 (sh)	296 (s) 289 (sh)	297 (s) 285 (sh, w)	Ligand (B)
259 (s) 242 (m)	245 (m) 235 (sh)	250 (sh) 244 (s)	245 (m) 236 (w)	Ligand (C)
	214 (s) 211 (sh)	216 (s) 212 (sh)	214 (s)	δ (N–Fe–N)
	191 (m) 176 (m)	192 (m) 176 (m)	197 (m) 178 (m)	Ligand (D)

As is seen in Figure 1, the corresponding Ni(II) and Zn(II) complexes show no bands in this region. Also, this region of the spectra is completely free from ligand absorption.

The free phen ligand absorbs at 432–411 (A) and 259–242 (C) cm^{-1}. In addition, all the three tris(phen) complexes studied show bands at 300–280 (B), 260–235 (C), and 200–160 (D) cm^{-1}. Thus these bands must be assigned to the ligand vibrations activated by complex formation. It was noted that the $[Fe(phen)_3]^{2+}$ ion exhibits bands of medium and strong intensity at 220–210 cm^{-1}. These bands do not appear in phen complexes of other metals. We have, therefore, tentatively assigned them to the N–Fe–N skeletal bending modes.

$[Ni(bipy)_3]^{2+}$ Ion. The infrared spectrum of the chloride was measured by Inskeep[4] and those of the chloride and bromide were measured by Clark and Williams.[5] In addition, we have obtained the spectra of the iodide, sulfate, and perchlorate. The spectra of isotopic species containing ^{58}Ni and ^{62}Ni have been obtained for the perchlorate and iodide. All the frequencies observed are listed in Table III.

As stated in a previous section, the bipy ligand vibrations appear in the regions 430–400 (A), 375–355 (B), 290–275 (C), 260–235 (D), 240–210 (E), and 195–160 (F) cm^{-1}. We have noted, however, that the three bands at 293.1, 282.9, and 267.3 cm^{-1} of $[^{58}Ni(bipy)_3](ClO_4)_2 \cdot 2H_2O$ and two bands at 282.2 and 259.1 cm^{-1} of $[^{58}Ni(bipy)_3]I_2 \cdot 6H_2O$ show exceptionally large shifts to lower frequencies (3.9–7.3 cm^{-1}) by the ^{58}Ni–^{62}Ni substitution. Thus, these bands must be assigned to the Ni–N stretching modes. The band at *ca.* 282 cm^{-1} is probably an overlap of the Ni–N stretching and the ligand vibration (C). The broadness of this band in the spectra of the halide and sulfate salts seems to support this interpretation. Previously, Inskeep[4] assigned the 286-cm^{-1} band of the chloride to the Ni–N stretching mode while Clark and Williams[5] assigned it to a ligand vibration.

$[Ni(phen)_3]^{2+}$ Ion. Table IV lists the observed frequencies of the chloride, iodide, and perchlorate. The ^{58}Ni–^{62}Ni isotope shifts have been studied for the iodide and perchlorate. As is seen in Figure 1, three bands between 302 and 243 cm^{-1} show large isotopic shifts, and can be assigned to the Ni–N stretching modes. These frequencies are close to those obtained for the $[Ni(bipy)_3]^{2+}$ ion (292–258 cm^{-1}) indicating that the strength of the Ni–N bonds of tris(phen) complexes is similar to that of tris(bipy) complexes. As stated previously, the phen ligand vibrations are expected to appear in the regions 300–280 (B) and 260–235 (C) cm^{-1}. These ligand vibrations are probably hidden under the Ni–N stretching bands. In fact, the bands near 300 cm^{-1} observed for the complexes are always broad (Figure 1). Previously, Inskeep[4] assigned the 299-cm^{-1} band of the chloride to the Ni–N stretching mode.

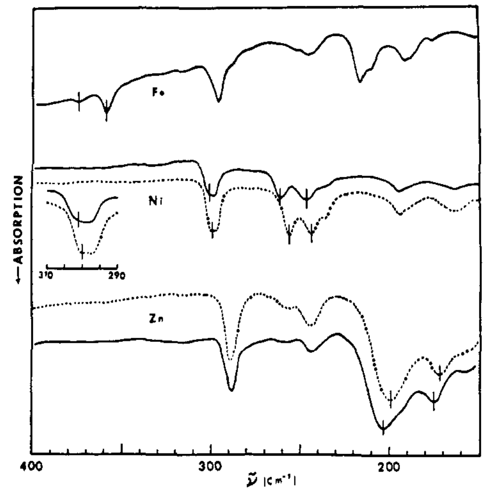

Figure 1. Far-infrared spectra of $[Fe(phen)_3](ClO_4)_2$ (natural abundance), $[Ni(phen)_3](ClO_4)_2 \cdot {}^1/_2H_2O$ (^{58}Ni, ———, and ^{62}Ni, – – – –), and $[Zn(phen)_3](ClO_4)_2$ (^{64}Zn, ———, and ^{68}Zn, – – – –). Vertical lines indicate the peak positions of the M–N stretching bands.

$[Zn(bipy)_3]^{2+}$ Ion. Table V lists the observed frequencies and band assignments for the two salts of the $[Zn(bipy)_3]^{2+}$ ion. Our isotopic study shows that only two bands at 235.0 and 186.0 cm^{-1} of $[^{64}Zn(bipy)_3]Cl_2 \cdot 7H_2O$ are sensitive to the ^{64}Zn–^{68}Zn substitution. Thus, they are assigned to the Zn–N stretching modes. The ligand vibrations (E and F) are probably hidden under these strong Zn–N stretching bands. Postmus, *et al.*,[9] have assigned the Zn–N stretching bands of $[Zn(bipy)X_2]$ (X = Cl, Br, and I) at 250–240 cm^{-1}.

$[Zn(phen)_3]^{2+}$ Ion. Table VI lists the observed frequencies and band assignments for the nitrate and perchlorate of the $[Zn(phen)_3]^{2+}$ ion. Our isotopic

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(9) C. Postmus, J. R. Ferraro, and W. Wozniak, *Inorg. Chem.*, **6**, 2030 (1967).

Table III. Observed Frequencies, Isotopic Shifts, and Band Assignments for $[Ni(bipy)_3]^{2+}$ Ion (cm^{-1})

$[Ni(bipy)_3]$-$Cl_2\cdot 6H_2O$			$[Ni(bipy)_3]$-$Br_2\cdot 6H_2O$		$[Ni(bipy)_3]\cdot SO_4$	$[Ni(bipy)_3]I_2\cdot 6H_2O^{a}$			$[Ni(bipy)_3](ClO_4)_2\cdot 2H_2O^{a,e}$			
						Ni	^{58}Ni	$\Delta\bar{\nu}^{d}$	Ni	^{58}Ni	$\Delta\bar{\nu}^{d}$	Assignment
440[b]	438 (w)[c]	438 (m)[a]	439 (vw)[c]	432 (w)[a]	439 (m)[a]	438 (w)	437.0	−1.4	439 (s)	438.4	−0.1	Ligand (A)
415	418 (w)	419 (m)	417 (w)	419 (w)	419 (m)	417 (m)	416.6	0.5	413 (s)	412.3	−0.2	
	367 (vw)	361 (w)	368 (vw)	374 (w)	360 (w)	358 (w)	*f*		359 (m)	359.0	−0.6	Ligand (B)
									292 (m)	293.1	*7.1*	ν (Ni–N)
286	278 (m)	281 (s, br)	282 (m)	282 (m, br)	282 (s, br)	282 (s, br)	282.2	*3.9*	282 (m)	282.9	*5.4*	ν (Ni–N) Ligand (C)
260		258 (m)		259 (w)	260 (w)	258 (w)	259.1	*5.0*	266 (m)	267.3	*7.3*	ν (Ni–N)
		g		*g*	*g*	*g*	*g*		256 (w)	257.3	0.0	Ligand (D)
		212 (w)		218 (m)		208 (m)	210.5		212 (w)	213.0	1.0	Ligand (E)
		182 (m)		183 (m)		181 (m)	181					
		169 (w)		169 (w)		169 (w)	169		164 (w)	164.0	0.5	Ligand (F)

[a] Present work. [b] Reference 4. [c] Reference 5. [d] $\Delta\bar{\nu}$ indicates an isotopic shift, $\bar{\nu}(^{58}Ni) - \bar{\nu}(^{62}Ni)$. [e] The perchlorate shows bands at 483, 468, and 458 cm^{-1} in addition to those listed above. [f] Too weak to be observed with a milligram scale sample. [g] Overlapped by the neighboring band.

Table IV. Observed Frequencies, Isotopic Shifts, and Band Assignments for $[Ni(phen)_3]^{2+}$ Ion (cm^{-1})

$[Ni(phen)_3]$-$Cl_2\cdot 7H_2O^{b}$	$[Ni(phen)_3]I_2\cdot 7H_2O^{a}$			$[Ni(phen)_3](ClO_4)_2\cdot {}^1/_2H_2O^{a,d}$			
	Ni	^{58}Ni	$\Delta\bar{\nu}^{c}$	Ni	^{58}Ni	$\Delta\bar{\nu}^{c}$	Assignment
425	425 (m)	425.0	0.0	426 (m)	425.5	−0.1	Ligand (A)
409, 393							
299 (s, br)	298 (s, br)	301.6	*3.3*	300 (s, br)	301.5	*2.3*	ν (Ni–N) Ligand (B)
256	255 (m)	256.3	*5.1*	260 (m)	260.2	*3.9*	ν (Ni–N)
	244 (m)	244.2	*2.2*	243 (m)	246.8	*2.8*	ν (Ni–N)
	237 (sh)	236.8	−0.5	238 (sh)	237.1	0.9	Ligand (C)
				192 (w)	192.8	−0.5	
	183 (m)	183.4	−1.2	188 (vw)	188.0	−0.5	Ligand (D)
				166 (m)	166.0	0.5	

[a] Present work. [b] Reference 4. [c] $\Delta\bar{\nu}$ indicates an isotopic shift, $\bar{\nu}(^{58}Ni) - \bar{\nu}(^{62}Ni)$. [d] The perchlorate shows a band at 482 cm^{-1}.

Table V. Observed Frequencies, Isotopic Shifts, and Band Assignments for $[Zn(bipy)_3]^{2+}$ Ion (cm^{-1})

$[Zn(bipy)_3]$-$(NO_3)_2\cdot 4H_2O$		$[Zn(bipy)_3]Cl_2\cdot 7H_2O$			
		Zn	^{64}Zn	$\Delta\bar{\nu}^{c}$	Assignment
433[b]	438 (m)[a]	433 (w)	433	0.0	Ligand (A)
415	418 (s)	418 (s)	419	0.0	
355	357 (m)	356 (w)	357.0	0.5	Ligand (B)
280	282 (vw)	288 (m)	288.3	0.3	Ligand (C)
	250 (sh)	247 (m)	248.0	0.0	Ligand (D)
	235 (s)	231 (s)	235.0	*2.5*	ν (Zn–N), Ligand (E)
	185 (s, br)	184 (s)	186.0	*3.5*	ν (Zn–N), Ligand (F)
	d	170 (w)	172.6	0.1	Ligand (F)

[a] Present work. [b] Reference 4. [c] $\Delta\bar{\nu}$ indicates an isotopic shift, $\bar{\nu}(^{64}Zn) - \bar{\nu}(^{68}Zn)$. [d] Hidden by the neighboring band.

Table VI. Observed Frequencies, Isotopic Shifts, and Band Assignments for $[Zn(phen)_3]^{2+}$ Ion (cm^{-1})

$[Zn(phen)_3]$-$(NO_3)_2\cdot 2H_2O$		$[Zn(phen)_3](ClO_4)_2$			
		Zn	^{64}Zn	$\Delta\bar{\nu}^{c}$	Assignment
	439 (vw)[a]	440 (vw)	441.0	0.0	Ligand (A)
422[b]	422 (s)	423 (s)	423.0	0.0	
407					
288	287 (s)	287 (s)	287.5	−0.5	Ligand (B)
262	260 (w)	260 (w)	260.0		Ligand (C)
	243 (m)	244 (m)	244.0	0.0	
	197 (s)	198 (s)	203.5	*4.0*	ν (Zn–N), Ligand (D)
	178 (m)	175 (m)	175.0	*3.0*	ν (Zn–N)
	160 (m)	160 (m)	160.0	0.0	Ligand (D)

[a] Present work. [b] Reference 4. [c] $\Delta\bar{\nu}$ indicates an isotopic shift, $\bar{\nu}(^{64}Zn) - \bar{\nu}(^{68}Zn)$.

study shows that two bands at 199.0 and 179.0 cm^{-1} of $[^{64}Zn(phen)_3](ClO_4)_2$ are shifted to lower frequencies by the ^{64}Zn–^{68}Zn substitution (Figure 1). Thus, these bands must be assigned to the Zn–N stretching modes. Although the phen complexes show a band of medium intensity at 244 cm^{-1}, this band is not sensitive to the metal isotope substitution and was, therefore, assigned to a ligand vibration (C). It is probable that the Zn–N stretching band at *ca.* 235 cm^{-1} observed for the corresponding tris(bipy) complex is hidden under this ligand vibration.

Summary

The complex ions, $[M(bipy)_3]^{2+}$ and $[M(phen)_3]^{2+}$, belong to D_3 symmetry. Thus, three M–N stretching modes (A_2 and 2E) are expected to be infrared active. However, we have observed two in some cases and three in other cases. It is not clear from the present study whether some of these bands are overlapped on each other or split due to the lowering of symmetry. The present isotopic studies show definitely that the M–N stretching bands of the Fe(II), Ni(II), and Zn(II) complexes are at *ca.* 375–360, 300–240, and 240–175 cm^{-1}, respectively. The order of masses of the three metals studied is Fe ≈ Ni < Zn. It is, therefore, safe to conclude that the present order of the M–N stretching frequencies, Fe(II) ≫ Ni(II) > Zn(II), represents the order of the strength of these M–N bonds. Previously, Inskeep[4] discussed the origin of this order from the electronic configurations of the metals involved.

In addition to the M–N stretching bands, these complex ions are expected to show the N–M–N bending bands in the low-frequency region. They are difficult to identify, however, since they give only small isotopic shifts (1.5–0.2 cm^{-1}).[10] As stated previously, the bands at 220–210 cm^{-1} of the Fe(II) complexes have been tentatively assigned to the N–Fe–N bending modes. The complexes of Ni(II) and Zn(II) may exhibit similar bands at much lower frequencies.

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Metal Isotope Effect on Metal–Ligand Vibrations. III. π-Allyl Complexes of Palladium(II)[1]

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Abstract: The infrared and Raman spectra of four Pd(II) π-allyl complexes have been measured from 4000 to 100 cm^{-1}. The far-infrared spectra of $[^{104}Pd(\pi\text{-}C_3H_5)Cl]_2$ and its ^{110}Pd analog have been obtained. From the observed isotopic shifts, the Pd–allyl stretching bands have been assigned at *ca.* 400 and 370 cm^{-1}. The Pd–Cl (bridging) and Pd–Br (bridging) stretching bands are located at *ca.* 260–240 and 190–170 cm^{-1}, respectively.

Studies of metal–olefin stretching vibrations are important in understanding the nature of metal–olefin bonds. Previously, we[2] have studied the metal–olefin stretching vibrations of monoolefin complexes with Pt(II) and Pd(II), and have shown that these monoolefin complexes exhibit one metal–olefin stretching band per metal–olefin bond unless the vibration is forbidden by the selection rule. It is, therefore, of particular interest to extend similar studies to metal–allyl complexes to determine the number of the metal–allyl stretching vibrations in infrared spectra.

The infrared spectra (4000–300 cm^{-1}) of Pd(II)–allyl complexes have been studied by Fritz.[3] He assigned the band at 401 cm^{-1} of $[Pd(\pi\text{-}C_3H_5)Cl]_2$ to the Pd–allyl stretching band. However, his assignments in the low-frequency region have been questioned by several investigators.[4,5] The infrared spectra of $[Pd(\pi\text{-}1\text{-}methylallyl)X]_2$ and $[Pd(\pi\text{-}2\text{-}methylallyl)X]_2$ (X = Cl and Br) down to 200 cm^{-1} have been reported by Lupin, *et al.*[4] However, no band assignments on the Pd–allyl stretching bands have been made by these investigators.

In the previous papers of this series,[6–8] we have demonstrated that the metal isotope technique is extremely useful in assigning the metal–ligand vibrations of a variety of coordination compounds. In this paper we have applied this technique to assign the Pd–allyl stretching modes of four π-allyl complexes of Pd(II).

Experimental Section

Preparation of Compounds. (1) **Di-μ-chloro-bis(π-allyl)dipalladium(II), $[Pd(\pi\text{-}C_3H_5)Cl]_2$.** This compound was prepared by the method of Smidt and Hafner.[9] Further recrystallization was carried out from benzene.

Anal. Calcd for $PdCl(C_3H_5)$: C, 19.7; H, 2.95; Cl, 19.4. Found: C, 20.8; H, 2.86; Cl, 19.3.

(2) **Di-μ-bromo-bis(π-allyl)dipalladium(II), $[Pd(\pi\text{-}C_3H_5)Br]_2$.** This complex was prepared by the method described by Lupin, *et al.*[4]

Anal. Calcd for $Pd(C_3H_5)Br$: C, 15.9; H, 2.22; Br, 35.2. Found: C, 15.8; H, 2.34; Br, 34.3.

(3) **Di-μ-chloro-bis(π-2-methylallyl)dipalladium(II), $[Pd(\pi\text{-}C_4H_7)Cl]_2$.** This complex was prepared by the method used by Dent, *et al.*[5] Further recrystallization was carried out from benzene.

Anal. Calcd for $Pd(C_4H_7)Cl$: C, 24.4; H, 3.58; Cl, 18.0. Found: C, 24.7; H, 3.76; Cl, 18.3.

(4) **Di-μ-bromo-bis(π-2-methylallyl)dipalladium(II), $[Pd(\pi\text{-}C_4H_7)Br]_2$.** This compound was prepared by the bromination of the chloro analog using the method of Lupin, *et al.*[4]

Anal. Calcd for $Pd(C_4H_7)Br$: C, 19.9; H, 2.92; Br, 33.1. Found: C, 20.0; H, 2.69; Br, 32.5.

Metal allyl complexes containing pure Pd isotopes were prepared on a milligram scale. In each case, metallic palladium (50 mg each) was converted into $Na_2[PdCl_4]\cdot 4H_2O$ and treated with the ligand using the method of Smidt and Hafner.[9] The purity of the isotopes was ^{104}Pd, 89.75%, and ^{110}Pd, 96.98%. The isotopes were purchased from Oak Ridge National Laboratory. The purity of each allyl complex was checked by comparing the spectrum with that reported in literature.[3,4]

Spectral Measurements. Infrared spectra were obtained on a Beckman IR 12 (4000–250 cm^{-1}) and a Hitachi Perkin-Elmer FIS-3 (400–33 cm^{-1}) spectrophotometer. The spectra between 4000 and 550 cm^{-1} were obtained in KBr pellets and those below 500 cm^{-1} were obtained as Nujol mulls sandwiched between polyethylene plates. The solution spectra were obtained by using polyethylene liquid cells (cell thickness, 1 and 2 mm).

The spectra of isotopic species were run with a scanning speed of 1-2 cm^{-1}/min. Reproducibility of the spectra was checked by running the spectra three to five times. The average error in fre-

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