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METAL ISOTOPE EFFECT ON METAL-LIGAND VIBRATIONS

V. *Cis* and *Trans* Ni(II) Phosphine-Halide Complexes†

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Infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) have been reported for $\text{Ni}(\text{DPE})\text{X}_2$ where X is Cl, Br and I and DPE is 1,2-bis(diphenylphosphino)ethane. The Ni-X and Ni-P stretching bands have been assigned based on the observed isotopic shifts due to the ^{58}Ni - ^{62}Ni substitution. The Ni-X stretching frequencies are always lower and the Ni-P stretching frequencies are always higher in the *cis*-complexes such as $\text{Ni}(\text{DPE})\text{X}_2$ than in the corresponding *trans*-complexes such as $\text{Ni}(\text{PEt}_3)_2\text{X}_2$. These differences between *cis* and *trans* configurations have been attributed to the strong *trans*-effect of phosphine ligands.

INTRODUCTION

According to Boorman and Carty,¹ the Ni-X (X = a halogen) stretching frequencies are very useful in distinguishing the *cis* and *trans* configurations of square-planar Ni(II) phosphine-halide complexes; the Ni-Cl stretching bands of the *trans*-complexes are at $407\text{--}403\text{ cm}^{-1}$ whereas those of the *cis*-complexes are at $330\text{--}313\text{ cm}^{-1}$. This marked difference in Ni-Cl stretching frequencies was attributed to the strong *trans*-effect of the phosphine ligand which is *trans* to the chlorine atom in the *cis*-complex. If so, the Ni-P stretching frequencies of the *cis*-complex would be higher than that of the *trans*-complex since the chlorine atom (ligand of relatively weak *trans*-effect) is *trans* to the phosphine ligand in the *cis*-complex. It is rather difficult, however, to assign the Ni-P stretching bands of these phosphine complexes unequivocally since their far-infrared spectra are too complicated to give an empirical interpretation. Boorman and Carty¹ suggest, by analogy with previous assignments by other workers^{2, 3}, either 335 or 426 cm^{-1} for the Ni-P stretching mode of *trans*- $\text{Ni}(\text{PPh}_2\text{Et})_2\text{Cl}_2$ ⁴. No Ni-P stretching bands could be assigned for *cis*-complexes such as $\text{Ni}(\text{DPE})\text{X}_2$ (DPE: 1,2-bis(diphenylphosphino) ethane) due to the complexity of the spectra. Although Hudson *et al.*⁵ obtained the far-infrared spectra of $\text{Ni}(\text{DPE})\text{X}_2$ (X = Cl or Br), they assigned only the Ni-X stretching bands.

In the previous papers of this series,⁶⁻⁹ we have demonstrated that the metal isotope technique¹⁰ is very useful in assigning the metal-ligand vibra-

tions of various coordination compounds. Indeed, this has led to new or re-assignments of many metal-ligand stretching vibrations in metal complexes. It is, therefore, of particular interest to assign the Ni-P and Ni-X stretching bands of Ni(II) phosphine-halide complexes of *cis* and *trans* configurations by this technique and to discuss the differences in spectra and bonding between these two configurations.

EXPERIMENTAL

Preparation of Compounds

All the DPE complexes were prepared according to the methods of Hudson *et al.*⁵ and Van Hecke and Horrocks.¹¹ *Trans*- $\text{Ni}(\text{PPh}_2\text{Et})_2\text{Cl}_2$ was prepared by the method of Jensen.¹² The ligand, DPE, was purchased from Strem Chemicals Inc., Danvers, Mass. Metal complexes containing pure metal isotopes were prepared on a milligram scale. The ^{58}Ni (99.98% pure) and ^{62}Ni (99.02% pure) isotopes were purchased from Oak Ridge National Laboratory. The purity of each complex was checked by comparing the spectrum with that of the corresponding complex containing the metal of natural abundance for which microanalyses shown below have been obtained.

The chloro complex exists in two forms; one form (reddish-orange, hereafter referred to as Form A) can be obtained from ethanol or methanol solution⁵ and the other (light orange, hereafter

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	Calcd.			Found		
	C%	H%	X%	C%	H%	X%
Ni(DPE)Cl ₂ (A)	59.2	4.7	13.5	59.8	5.1	13.4
Ni(DPE)Cl ₂ (B)	59.2	4.7	13.5	57.7	4.8	13.5
Ni(DPE)Br ₂	50.6	4.3	25.9	50.3	4.1	25.2
Ni(DPE)I ₂	43.9	3.4	35.6	43.8	3.4	35.9

referred to as Form B) can be precipitated from a solution containing 2:1 molar mixture of 2-propanol and methanol.¹¹ The spectrum of Form A agrees with that reported by Hudson *et al.*⁵ whereas the spectrum of Form B is identical with that of Boorman and Carty¹ in the far-infrared region.

Spectral measurements

Infrared spectra were measured on a Beckman IR 12 (4000–250 cm⁻¹) and a Hitachi-Perkin-Elmer FIS 3 (410–33 cm⁻¹) infrared spectrophotometer. The nujol mull with polyethylene plates was used to obtain the spectra of solid samples. The spectra were run with a scanning speed of 1 ~ 2 cm⁻¹/min. Reproducibility of the spectra was checked by multiple scans over the desired frequency range. The average error in frequency reading was ± 0.3 cm⁻¹. Calibration of frequency reading was made with polystyrene film, 1,2,4,-trichlorobenzene, and water vapor.

RESULTS AND DISCUSSION

Ni(DPE)X₂ Series

A series of complexes of the type Ni(DPE)X₂ are known to be *cis*-square-planar.^{1, 5, 11, 13} Then, two Ni-X and Ni-P stretching bands should be infrared active. Furthermore, these four skeletal vibrations are expected to be sensitive to the ⁵⁸Ni-⁶²Ni substitution. Figure 1 gives an actual tracing of the far-infrared spectra of ⁵⁸Ni(DPE)X₂ (X = Cl, Br, and I) and their ⁶²Ni analogs. Table I lists the observed frequencies, isotopic shifts, and probable band assignments. (The bands above 400 cm⁻¹ are not listed since they are not sensitive to metal isotope substitution.)

As stated previously, the chloro complex exists in two forms. In the high frequency region, Form A shows many more bands than Form B; some bands common to both forms are split into two bands in Form A. The spectrum of Form B is similar to those of Ni(DPE)Br₂ and Ni(DPE)I₂ which were not isolated in two forms. These data seem to indicate that the symmetry of the chelate ring (including four phenyl rings) is higher in Form B than in Form A. It is not clear, however, whether this difference is due to the rotational isomerism observed for 1,2-disubstituted ethanes (*cis* and *gauche* conformations of the chelate ring)¹⁴ or the differences in orientation of phenyl groups

TABLE I

Infrared frequencies, isotopic shifts and band assignments for Ni(DPE)X₂ (cm⁻¹)

DPE	⁵⁸ Ni(DPE)Cl ₂ (A)		⁵⁸ Ni(DPE)Cl ₂ (B)		⁵⁸ Ni(DPE)Br ₂	⁵⁸ Ni(DPE)I ₂		Assignment	
	$\bar{\nu}$	$\Delta\bar{\nu}^b$	$\bar{\nu}$	$\Delta\bar{\nu}^b$		$\Delta\bar{\nu}^b$	$\bar{\nu}$		$\Delta\bar{\nu}^b$
399 (m)	392.2 (m)	1.1	397.9 (m)	0.0	394.5 (w)	0.1	390.3 (w)	0.0	Ligand
—	378.9 (w)	2.7	380.2 (w)	2.8	385.0 (w)	-0.2	352.9 (s)	1.6	Ni-P stretch
—	341.3 (s)	1.8	332.5 (s)	4.5	365.0 (m)	2.8	259.5 (m)	2.5	Ni-X stretch
—	327.7 (s)	4.1	317. (sh)	—	289.7 (s)	5.1	212.0 (sh)	1.5	Ni-X stretch
337 (m)	(hidden)	} c	323 (s)	—	266.1 (s)	2.1	317.0 (w)	0.0	Ligand
—	(hidden)		(hidden)	—	326.4 (m)	0.1	277.6 (m)	4.1	Ni-P stretch
282 (w)	270 (m)		274.0 (w)	0.0	308.4 (m)	4.3	(hidden)		Ligand
260 (w)	250 (w)		263.7 (w)	0.0	(hidden)		251.6 (m)	0.0	
215 (w)	234.0 (m)	0.4	228.8 (m)	0.8	214.9 (m)	-0.2	217.8 (m)	0.0	Ligand
—	224.5 (m)	0.2	—	—	—	—	—	—	—
200 (w)	218.2 (sh)	0.0	210.0 (m)	0.0	204.9 (m)	0.1	(hidden)		Ligand

^a Form A exhibits a band at 288.2 cm⁻¹ ($\Delta\bar{\nu} = 0.2$ cm⁻¹) in addition to those listed above.

^b Isotopic shifts, $\bar{\nu}(\text{⁵⁸Ni}) - \bar{\nu}(\text{⁶²Ni})$.

^c Only tentative assignments are given here because of possible overlapping of the bands.

Intensity designation: sh, strong; m, medium; w, weak; sh, shoulder.

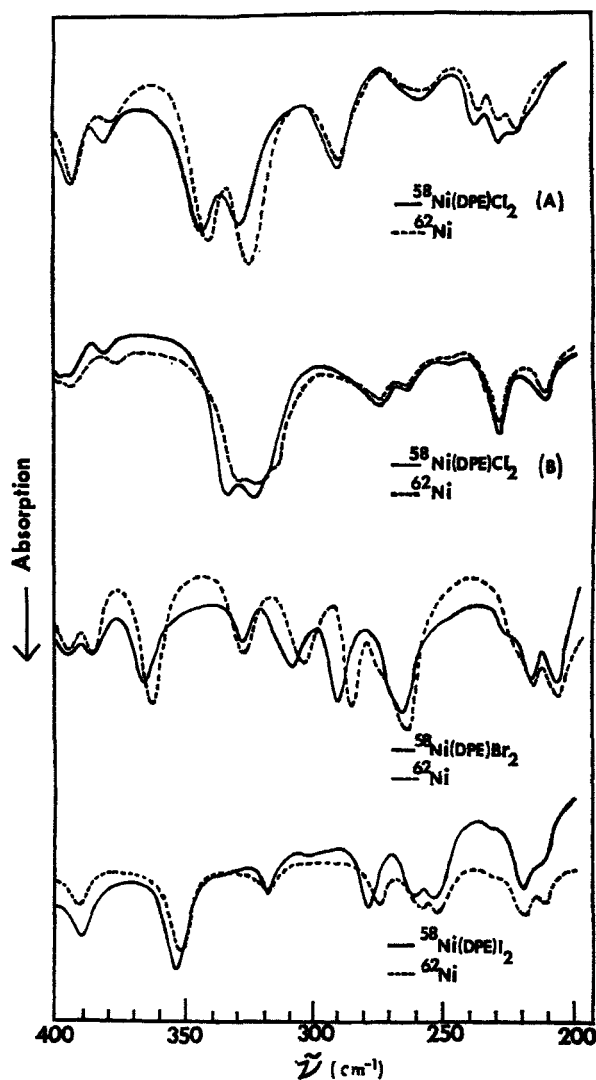


FIGURE 1 Far-infrared spectra of $^{58}\text{Ni}(\text{DPE})\text{X}_2$ ($\text{X} = \text{Cl}$, Br and I) and their ^{62}Ni analogs.

with both forms having the same chelate-ring conformation (for example, *gauche*).

a Ni-X stretching frequencies As is seen in Figure 1, both chloro complexes exhibit two or three bands in the region from 341 to 317 cm^{-1} . These bands are relatively strong and absent in the bromo and iodo analogs. Furthermore, they are sensitive to the ^{58}Ni - ^{62}Ni substitution. In agreement with previous investigations,^{1,5} it is most reasonable to assign them to the Ni-Cl stretching bands of *cis*-

complexes.[†] However, both bromo and iodo complexes show a ligand vibration in this region (326.4 and 317.0 cm^{-1} , respectively). In the case of the chloro complex, the corresponding ligand vibration is probably hidden under these Ni-Cl stretching bands.

In the previous paper of this series,⁶ we have shown that the Ni-Cl and Ni-Br stretching bands of *trans*- $^{58}\text{Ni}(\text{PEt}_3)_2\text{Cl}_2$ and *trans*- $^{58}\text{Ni}(\text{PEt}_3)_2\text{Br}_2$ are at 403.3 and 337.8 cm^{-1} , respectively. The ratio $\bar{\nu}(\text{Ni-Br})/\bar{\nu}(\text{Ni-Cl})$ is 0.84 in this case. If a similar frequency ratio is preserved for *cis*-complexes, one might expect the Ni-Br stretching bands of $\text{Ni}(\text{DPE})\text{Br}_2$ at around 276 cm^{-1} [(341 + 317)/2 \times 0.84]. As is seen in Figure 1 and Table 1, the bromo complex exhibits four bands at ca. 365, 308, 290, and 266 cm^{-1} which are sensitive to the metal isotope substitution. It is, therefore, reasonable to assign the 290 and 266 cm^{-1} bands to the Ni-Br stretching bands. The present assignments are in agreement with Hudson *et al.*⁵ but different from those of Boorman and Carty¹ who gave 264 and 250 (shoulder band) cm^{-1} as the Ni-Br stretching frequencies.

The iodo complex exhibits four bands at ca. 353, 278, 260, and 212 cm^{-1} which give relatively large shifts by the ^{58}Ni - ^{62}Ni substitution. Since the Ni-I stretching frequency should be lower than the Ni-Br stretching frequency, it is reasonable to assign the latter two bands to the Ni-I stretching modes.

b Ni-P stretching frequencies As stated before, the bromo complex exhibits four bands at ca. 365, 308, 290, and 266 cm^{-1} which are shifted to lower frequencies by the ^{58}Ni - ^{62}Ni substitution. The latter two bands have already been assigned to the Ni-Br stretching modes. Then the former two bands at 365 and 308 cm^{-1} arise most probably from the Ni-P stretching modes. The order of the *trans*-effect is $\text{Cl} < \text{Br} < \text{I}$. Thus the Ni-P bond is expected to be the strongest in the chloro complex and the weakest in the iodo complex. If so, it is most reasonable to assign two metal-isotope

[†] These Ni-Cl stretching modes may couple with the Ni-P stretching modes. It is rather difficult, however, to discuss the degree of vibrational coupling without rigorous normal coordinate analysis. In the present work, we assume that the degree of coupling is not serious enough to obscure the identity of each mode. This interpretation is supported by the discussions on relative intensity and frequency ratio on the Ni-X stretching modes in the text.

sensitive bands of the iodo complex at ca. 353 and 278 cm^{-1} to the Ni-P stretching modes.

The Ni-P stretching frequencies of the chloro complex are expected to be higher than those of the bromo complex. Both forms of the chloro complex exhibit a weak band near 380 cm^{-1} which shifts to a lower frequency by ca. 2.7 cm^{-1} by the ^{58}Ni - ^{62}Ni substitution. Thus, this band is assigned to one of the Ni-P stretching modes. The other Ni-P stretching band is most probably hidden under the Ni-Cl stretching bands at 341-317 cm^{-1} . As stated previously, a ligand vibration is also expected to appear in this region. Thus the spectra of the chloro complexes in the 341-317 cm^{-1} region are due to overlap of several bands. Only the tentative assignments are listed in Table I.

Trans-Ni(II) Phosphine-Halide Series

The *trans*-complexes containing ligands similar to DPE are of the types *trans*-Ni(PPh₂R)₂X₂ and *trans*-Ni(PR₃)₂X₂ where R is an alkyl group. The observed frequencies of *trans*-Ni(PPh₂Et)₂Cl₂ (^{58}Ni and ^{62}Ni) are listed in Table II together with those obtained for *trans*-Ni(PEt₃)₂Cl₂ (^{58}Ni and ^{62}Ni) in our previous study.⁶ Theoretically, one Ni-Cl and one Ni-P stretching vibration are infrared active for these complexes. Furthermore, they are expected to give large shifts relative to other bands when ^{58}Ni is substituted by ^{62}Ni . Table II clearly indicates that two bands at 403-401 and 273-252 cm^{-1} are sensitive to the metal isotope substitution. As discussed in our previous paper,⁶ the former is assigned to the Ni-Cl stretching whereas the latter is attributed to the Ni-P stretching.

According to Hayter and Humic,¹⁵

Ni(PPh₂Et)₂Br₂ exists either as a planar or a tetrahedral complex. However, its planar form is too unstable to measure the spectrum. As Table II shows, the Ni-Cl and Ni-P stretching frequencies of Ni(PPh₂Et)₂Cl₂ are very similar to those of Ni(PEt₃)₂Cl₂. Thus the Ni-Br and Ni-P stretching frequencies of *trans*-Ni(PPh₂Et)₂Br₂ may be close to those of *trans*-Ni(PEt₃)₂Br₂ (ca. 338 and 265 cm^{-1} , respectively).⁶

Ni(PPh₂Et)₂I₂ exists only in a tetrahedral form.¹⁵ Furthermore, *trans*-Ni(PEt₃)₂I₂ is too unstable to measure the spectrum. In Table II, we have listed the frequencies of *trans*-Ni(PPhMe₂)₂I₂ obtained by Boorman and Carty.¹ These authors assigned the Ni-P and Ni-I stretching bands at 424 and 255 cm^{-1} , respectively. The band assignments listed in Table II were made, however, based on our metal-isotope studies on analogous chlorides and bromides.

Comparison of Ni-X and Ni-P Stretching Frequencies between Cis and Trans Configurations

Table III summarizes the Ni-X and Ni-P stretching frequencies of planar complexes obtained in this work together with those of tetrahedral PPh₃ complexes. It is seen that the Ni-X stretching frequencies scatter over a wide frequency region depending upon the structure of the Ni(phosphine)₂X₂ type molecule: Ni-Cl stretching, 401 ~ 305 cm^{-1} ; Ni-Br stretching, 338 ~ 232 cm^{-1} ; Ni-I stretching 260 ~ 212 cm^{-1} . There are marked differences in Ni-X stretching frequencies of the *cis* and *trans*-configurations. The Ni-X stretching frequencies of

TABLE II

Infrared frequencies, isotopic shifts and band assignments for *trans*-Ni(II) phosphine-halide complexes (cm^{-1})

$^{58}\text{Ni}(\text{PPh}_2\text{Et})_2\text{Cl}_2$		$^{58}\text{Ni}(\text{PEt}_3)_2\text{Cl}_2^a$		$^{58}\text{Ni}(\text{PEt}_3)_2\text{Br}_2^a$		$\text{Ni}(\text{PPhMe}_2)_2\text{I}_2^b$	Assignment
$\bar{\nu}$	$\Delta\bar{\nu}^c$	$\bar{\nu}$	$\Delta\bar{\nu}^c$	$\bar{\nu}$	$\Delta\bar{\nu}^c$	$\bar{\nu}$	
424.9 (m)	0.0	416.7 (m)	0.0	413.6 (m)	1.2	424 (s)	Ligand
400.8 (s)	6.3	403.3 (vs)	6.7	337.8 (m)	10.5	260 (m)	Ni-X stretch
341.6 (s)	0.4	372.5 (m)	-0.1	374.0 (m)	1.1	373 (m)	Ligand
						366 (m)	
302.7 (w)	0.2	329.0 (m)	-0.5	327.8 (s)	0.5	300 (m)	Ligand
251.9 (m)	4.6	273.4 (m)	5.9	265.0 (m)	4.7	252 (m)	Ni-P stretch
224.2 (m)	0.4	200.2 (m)	0.8	190.4 (s)	0.7		Ligand

^a Taken from Ref. 3.

^b These frequencies were provided by A. J. Carty. However, band assignments were made by the present authors.

^c $\bar{\nu}(^{58}\text{Ni}) - \bar{\nu}(^{62}\text{Ni})$

Intensity designation: vs, very strong; s, strong; m, medium; w, weak.

TABLE III

Comparison of Ni-X and Ni-P stretching frequencies between various configurations (cm⁻¹)

	<i>trans</i> - ⁵⁸ Ni(PR ₂ R') ₂ X ₂		<i>cis</i> - ⁵⁸ Ni(DPE)X ₂		tet-Ni(PPh ₃) ₂ X ₂	
	$\nu(\text{Ni-X})$	$\nu(\text{Ni-P})$	$\nu(\text{Ni-X})$	$\nu(\text{Ni-P})$	$\nu(\text{Ni-X})$	$\nu(\text{Ni-P})$
X = Cl	401 ^a	252 ^a	341 } ^d 328 }	379 } ^d — }	341 } ^e 305 }	190 } ^e 164 }
Br	338 ^b	265 ^b	290 } 266 }	365 } 308 }	265 } ^f 232 }	193 } ^f 184 }
I	260 ^c	252 ^c	260 } 212 }	353 } 278 }	215 ^f 198 }	198 } ^f 182 }

^a R = Ph, R' = Et ^b R = R' = Et (Ref. 3) ^c R = CH₃, R' = Ph (natural abundance Ni) ^d Form A (see text) ^e ⁵⁸Ni complex (Ref. 3) ^f Ref. 1.

the *cis*-complex are always lower than those of the corresponding *trans*-complex, since the Ni—X bond is *trans* to the Ni—P bond in the *cis*-complex. A similar trend was found by Park and Hendra¹⁶ for a pair of *cis*- and *trans*-Pd(PMe₃)₂X₂ where X is Cl or Br. For example, the Pd-Cl stretching of the *trans*-complex is at 358 cm⁻¹ whereas those of the *cis*-complex are at 297 and 272 cm⁻¹. This is true, however, only for complexes containing a ligand of strong *trans*-effect such as phosphines. In fact, there are no marked differences in Pd-Cl stretching frequencies of *cis*- and *trans*-Pd(NH₃)₂Cl₂ (327 and 306 cm⁻¹ for *cis*- and 333 cm⁻¹ for *trans*-complex)¹⁷ because NH₃ does not exert a strong *trans*-effect on the Pd-Cl bond. On the contrary, the Ni-P stretching frequencies of the *cis*-complex are always higher than those of the corresponding *trans*-complex since the Ni—P bond is *trans* to the Ni—X bond in the *cis*-complex and to the Ni—P bond in the *trans*-complex.

As expected from the order of *trans*-effect of halogens, the Ni-P stretching frequencies are the highest in Ni(DPE)Cl₂ and the lowest in Ni(DPE)I₂. It was also noted that the separation of two Ni-P stretching bands is relatively large (55 ~ 75 cm⁻¹) in the Ni(DPE)X₂ series. Similar trends have been observed for many other chelate ring compounds. This is probably due to the fact that other groups constituting a chelate ring (phenyl and methylene groups in this case) exert repulsive forces which help separate two metal-ligand bond stretching frequencies.¹⁸

In the *trans*-series, the Ni-P stretching frequencies are relatively independent from the nature of a halogen since two Ni—P bonds are *trans* to each other.

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