

Metal Isotope Effect on Metal-Ligand Vibrations.

IV. Metal Complexes of Acetylacetonone¹

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Abstract: In order to assign the metal-oxygen stretching bands of acetylacetonato complexes, infrared spectra (800–100 cm⁻¹) have been measured for isotopic pairs of Fe(acac)₃ (⁵⁴Fe and ⁵⁷Fe), Cr(acac)₃ (⁵⁰Cr and ⁵³Cr), Pd(acac)₂ (¹⁰⁴Pd and ¹¹⁰Pd), Cu(acac)₂ (⁶³Cu and ⁶⁵Cu), *trans*-Ni(acac)₂(pyridine)₂, and [Ni(acac)₂]₃ (⁵⁸Ni and ⁶²Ni). The metal-oxygen stretching bands assigned by normal coordinate analysis show large isotopic shifts relative to other bands. Previously, the Cr-O stretching bands of Cr(acac)₃ had been assigned from the isotopic shifts due to an ¹⁶O-¹⁸O substitution. Present results show that these assignments are erroneous.

In 1960, Nakamoto and Martell² carried out a normal coordinate analysis on the 1:1 (metal/ligand) model of bis(acetylacetonato)copper (abbreviated as Cu(acac)₂). Subsequently, similar calculations were extended to acetylacetonato complexes of other transition metals.³ In these 1:1 model calculations, two metal-oxygen (M-O) stretching bands were assigned at *ca.* 470–420 and 320–250 cm⁻¹ although the latter bands were not observed at that time. Since then, a number of investigators^{4–8} have measured the far-infrared spectra of acetylacetonato complexes. Mikami, *et al.*,⁸ carried out rigorous normal coordinate treatments on 1:2 (square-planar) and 1:3 (octahedral) models. Their calculations provided more detailed and reliable band assignments in the low-frequency region than those obtained from 1:1 model calculations. For example, their calculations show that several vibrations in the low-frequency region contain M-O stretching character to a varying degree through vibrational coupling. Thus far, the only experimental evidence to support these assignments has been the observation that the M-O stretching bands are metal sensitive; they are shifted to higher or lower frequencies by changing the metal in a series of compounds having the same structure. It is now possible to provide more direct evidence to confirm these theoretical assignments by comparing the spectra of a pair of metal complexes in which only the metal is isotopically substituted.⁹ In this paper, we have applied this metal isotope technique to Fe(acac)₃, Cr(acac)₃, Pd(acac)₂, Cu(acac)₂, *trans*-Ni(acac)₂(pyridine)₂, and [Ni(acac)₂]₃.

Experimental Section

Preparation of Compounds. All metal acetylacetonato complexes containing metal isotopes were prepared on a milligram scale using

(1) This work was supported by an ACS-PRF unrestricted research grant (3318-C3,5).

(2) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

(3) (a) K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 1066 (1961); (b) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *ibid.*, **83**, 1272 (1961).

(4) K. E. Lawson, *Spectrochim. Acta*, **17**, 248 (1961).

(5) J. P. Dismukes, L. H. Jones, and J. C. Ballar, Jr., *J. Phys. Chem.*, **65**, 792 (1961).

(6) R. D. Gillard, H. G. Silver, and J. L. Wood, *Spectrochim. Acta*, **20**, 63 (1964).

(7) S. Pinchas, B. L. Silver, and I. Laulicht, *J. Chem. Phys.*, **46**, 1506 (1967).

(8) M. Mikami, I. Nakagawa, and T. Shlmanouchi, *Spectrochim. Acta*, **23A**, 1037 (1967).

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

literature methods.¹⁰ Metal isotopes were purchased from Oak Ridge National Laboratory. The purity of each metal isotope was ⁵⁴Fe (98.19%), ⁵⁷Fe (90.73%), ⁵⁰Cr (89.01%), ⁵³Cr (96.40%), ¹⁰⁴Pd (89.75%), ¹¹⁰Pd (96.98%), ⁶³Cu (99.62%), ⁶⁵Cu (99.70%), ⁵⁸Ni (99.98%), and ⁶²Ni (99.02%). Acetylacetonone was purchased from the Aldrich Chemical Co., Milwaukee, Wis. The purity of each complex was checked by comparing the spectrum with that reported in the literature.^{2–8}

Spectral Measurements. Infrared spectra were measured on a Beckman IR-12 (4000–200 cm⁻¹) and a Hitachi-Perkin-Elmer FIS-3 (400–33 cm⁻¹) infrared spectrophotometer. The Nujol mull technique with CsI plates (800–400 cm⁻¹) or polyethylene plates (400–33 cm⁻¹) was employed for all complexes except Fe(III) and Cr(III) complexes for which the KBr pellet technique was used to obtain the spectra above 300 cm⁻¹. The spectra were run on an expanded-frequency scale 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.

Results and Discussion

Fe(acac)₃. Figure 1 shows an actual tracing of infrared spectra (470–180 cm⁻¹) of ⁵⁴Fe(acac)₃ and its ⁵⁷Fe analog. Table I lists the observed frequencies and band assignments obtained by three groups of investigators. The band assignments by Nakamoto, *et al.*,^{3a} and Mikami, *et al.*,⁸ are based on normal coordinate analyses on the 1:1 and 1:3 models, respectively. However, the origin of the band assignments by Gillard, *et al.*,⁶ is not clear. Nevertheless, these three groups of investigators agree in assigning the bands at *ca.* 435 and 300 cm⁻¹ to the Fe-O stretching modes. Our isotope study further confirms these assignments since both bands show large shifts relative to other bands (Table I). The isotopic shift of the 435-cm⁻¹ band (1.5 cm⁻¹) is much smaller than that of the 300-cm⁻¹ band (5.5 cm⁻¹). This result indicates that the 435-cm⁻¹ band is a coupled vibration between Fe-O and C-CH₃ stretching modes as suggested by Mikami, *et al.*

Theoretically, three Fe-O stretching modes (A₂ and 2E) are infrared active under the D₃ symmetry of the Fe(acac)₃ molecule. According to Mikami, *et al.*, the bands at 435 and 300 cm⁻¹ belong to the E and A₂ species, respectively. They have calculated the frequency of the third Fe-O stretching band to be 222 cm⁻¹ (E). It was not possible to confirm the isotopic shift of this band since it is partially overlapped by the ring deformation at 202 cm⁻¹.

(10) "Inorganic Syntheses," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1957, p 105.

Table I. Observed Frequencies, Band Assignments, and Isotopic Shifts for $\text{Fe}(\text{acac})_3$ (cm^{-1})^a

Nakamoto, <i>et al.</i> ^{3a}	Gillard, <i>et al.</i> ⁶	Mikami, <i>et al.</i> ⁸	Present work	
			⁵⁴ Fe	Shift ^b
800 } π (CH)		801 } π (CH)	802.5	0.0
770 } π (CH)		780 } π (CH)	780.0	0.0
663, ring + $\nu(\text{FeO})$	770, ring	771 } π (CH)	772.8	0.0
	663, ring	671 } ring	668.0	0.0
		667 } ring		
654, $\delta(\text{CR}) + \nu(\text{FeO})$	654, ?	656, $\pi(\text{RCCO})$	654.5	0.5
559 } π ?	559 } ring	559 } ring	562.0	0.5
549 } π ?	549 } ring	548 } ring	551.3	0.2
434, $\nu(\text{FeO})$	434, $\nu(\text{FeO})$	433, $\nu(\text{FeO}) + \nu(\text{CR})$	436.0	1.5
411, ?	411, ?	415 } ring	415.5	0.0
		408 } ring	408.0	0.0
(373), ring				
(273), $\nu(\text{FeO})$	289, $\nu(\text{FeO})$	298, $\nu(\text{FeO})$	300.5	5.0
(265), $\delta(\text{CR})$		(222), $\nu(\text{FeO}) + \nu(\text{CR})$		
(199), ring		202, ring	202.0	0.0
	111, $\pi(\text{ring})$	(162), ring	166.0	

^a Abbreviations: ν , stretching; δ , in-plane bending; π , out-of-plane bending; ring, ring deformation; M, metal; R, CH_3 . Numbers in brackets indicate calculated frequencies. These abbreviations were used in Tables I–V. Band assignments: vibrational coupling is shown by + signs between individual modes. ^b $\bar{\nu}(\text{}^{54}\text{Fe}) - \bar{\nu}(\text{}^{57}\text{Fe})$.

Table I indicates that three bands between 660 and 540 cm^{-1} show small isotopic shifts (0.5–0.2 cm^{-1}). Although the magnitude of these shifts is close to the limit of experimental errors, they have been observed consistently through several measurements. Thus,

the bands at 654.5 and 561.0 cm^{-1} of the ⁵⁴Fe complex probably contain a small amount of Fe–O stretching character as suggested by previous investigators.^{3a,8} A more detailed discussion of these band assignments cannot be made until the observed isotopic shifts are compared with theoretical values obtained from a rigorous normal coordinate analysis.

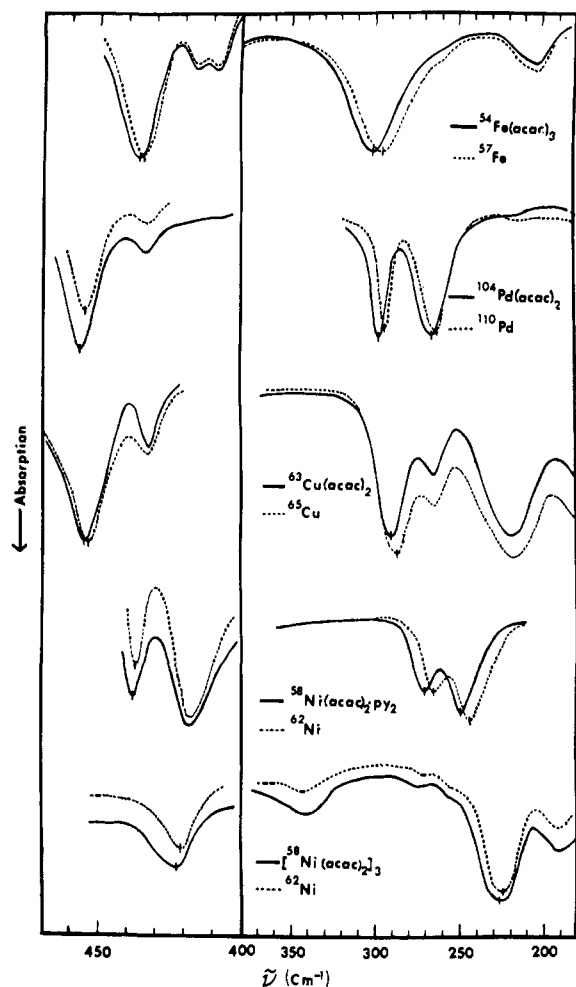


Figure 1. Far-infrared spectra of $\text{Fe}(\text{acac})_3$, $\text{Pd}(\text{acac})_2$, $\text{Cu}(\text{acac})_2$, $\text{Ni}(\text{acac})_2(\text{pyridine})_2$, and $[\text{Ni}(\text{acac})_2]_3$ containing metal isotopes.

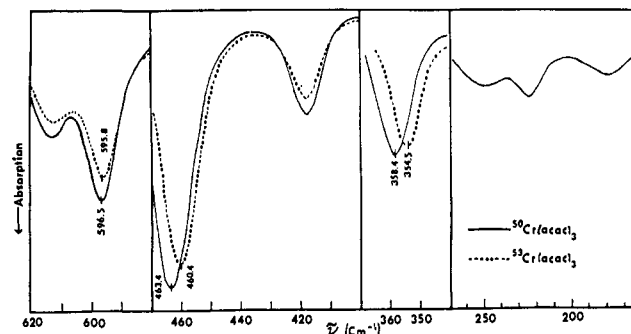


Figure 2. Infrared spectra of ⁵⁰Cr(*acac*)₃ and its ⁵³Cr analog.

Cr(*acac*)₃. Figure 2 shows an actual tracing of the infrared spectra of ⁵⁰Cr(*acac*)₃ and its ⁵³Cr analog. Table II lists the observed frequencies, band assignments, and isotopic shifts. The band assignments of Pinchas, *et al.*,⁷ are based on the observed isotopic shifts due to an ¹⁶O–¹⁸O substitution. As shown in Table II, the band at 592 cm^{-1} gives the largest isotopic shift (19 cm^{-1}). Thus, Pinchas, *et al.*, assigned this band to a pure Cr–O stretching mode. On the other hand, our ⁵⁰Cr–⁵³Cr experiment shows that the same band gives a shift of only 0.7 cm^{-1} which is much smaller than that of the 463 (3.0 cm^{-1}) or the 358 (3.9 cm^{-1}) band. This result definitely shows that the 592- cm^{-1} band cannot be assigned to a pure Cr–O stretching mode. As suggested earlier by Nakamoto, *et al.*, the 463- cm^{-1} band must be assigned to a relatively pure Cr–O stretching mode. The 358- cm^{-1} band gives the largest isotopic shift due to the ⁵⁰Cr–⁵³Cr substitution, and will probably correspond to the 300- cm^{-1} band of $\text{Fe}(\text{acac})_3$. Since the masses of Fe and Cr are

Table II. Observed Frequencies, Band Assignments, and Isotopic Shifts for Cr(acac)₃ (cm⁻¹)

Nakamoto, <i>et al.</i> ^{3a}	Gillard, <i>et al.</i> ⁶	Pinchas, <i>et al.</i> ⁷	Shift ^a	Present work	
				⁵⁰ Cr	Shift ^b
788 } π(CH)		801 } π(CH)		791.5	0.0
772 } π(CH)		776 } π(CH)		776.0	0.0
677, ring + ν(CrO)	772, ring	776, π(CH)		772.0	0.0
658, δ(CR) + ν(CrO)	677, ring	678, ring + ν(CrO)	11	681.0	0.5
609 } π ?	658, ?	661, π	3	659.5	0.0
594 } π ?	609 } ring			613.2	1.0
459, ν(CrO)	594 } ring	592, ν(CrO)	19	596.5	0.7
416, π ?	459, ν(CrO)	456, δ(CR) + ν(CrO)	5	463.4	3.0
(373), ring	416, ?	416, δ(OCrO)	8	417.8	0.0
(307), ν(CrO)				358.4	3.9
(277), δ(CR)	355, ν(CrO)			250.0 ^c	
(202), ring				224.0 ^c	
	103, π(ring)			179.0 ^c	

^a $\bar{\nu}(^{16}\text{O}) - \bar{\nu}(^{18}\text{O})$. ^b $\bar{\nu}(^{50}\text{Cr}) - \bar{\nu}(^{53}\text{Cr})$. ^c Natural abundance: the spectra of the complexes containing pure metal isotopes were not obtained below 300 cm⁻¹ because the amount of the sample available was not sufficient to run the Nujol mull spectrum on our instrument.

Table III. Observed Frequencies, Band Assignments, and Isotopic Shifts for Pd(acac)₂ (cm⁻¹)

Nakamoto, <i>et al.</i> ^{3b}	Mikami, <i>et al.</i> ⁸	Present work	
		¹⁰⁴ Pd	Shift ^a
781, π(CH)	786 } π(CH)	787.2	-0.2
	779 } π(CH)	780.6	0.2
697, ring + ν(PdO)	700, ν(CR), + ring + ν(PdO)	699.5	0.1
676, δ(CR) + ν(PdO)	678, π(RCCO)	677.8	1.3
659, π ?	661, ring + ν(PdO)	661.2	0.0
464, ν(PdO)	463, ν(PdO) + ν(CR)	466.8	1.5
442, π ?	441, ring	443.5	0.0
(373) ring			
(317), ν(PdO)	294, ν(PdO)	297.1	3.6
(268), δ(CR)	263, δ(CR) + ν(PdO), ring	265.9	2.9
(186), ring	(220), π (ring)		
	(174), π (ring)	173.0	0.0
	(105), τ(R) ^b	98.0	0.0

^a $\bar{\nu}(^{104}\text{Pd}) - \bar{\nu}(^{110}\text{Pd})$. ^b τ, torsional mode.

similar, these results may suggest that the stretching force constant of the Cr–O bond is much larger than that of the Fe–O bond.

The results of an isotopic substitution on the α-atom of the ligand (atom directly bonded to a metal) such as that made by Pinchas, *et al.*, must be interpreted with caution since the M–O stretching vibrations as well as ligand vibrations involving the motion of the α-atom (oxygen) are affected. It is, therefore, not possible to assign uniquely the metal–ligand stretching vibration by this method. The 592-cm⁻¹ band is probably due to an out-of-plane ring deformation in which the oxygen atom is displaced appreciably.

Pd(acac)₂. Figure 1 shows the infrared spectra of ¹⁰⁴Pd(acac)₂ and its ¹¹⁰Pd analog. Table III lists the observed frequencies and band assignments by Nakamoto, *et al.*,^{3b} and Mikami, *et al.*⁸ The results of the present isotopic study are also included in the same table.

Theoretically, only two Pd–O stretching vibrations (B_{1u} and B_{2u}) should be infrared active under D_{2h} symmetry of the Pd(acac)₂ molecule. Thus, only these two bands are expected to be sensitive to an isotopic substitution if no vibrational coupling exists between M–O stretching and other modes. Table III shows, however, that four bands at 677.8, 466.8, 297.1, and 265.9 cm⁻¹ of ¹⁰⁴Pd(acac)₂ are shifted to lower frequencies by the ¹⁰⁴Pd–¹¹⁰Pd substitution. This result indi-

cates that these four bands must contain the Pd–O stretching character.

According to Mikami, *et al.*,⁸ the 466.8- (B_{1u}) and 265.9-cm⁻¹ (B_{3u}) bands are due to coupled vibrations involving the Pd–O stretching modes, and the 297.1-cm⁻¹ (B_{2u}) band is due to a pure Pd–O stretching vibration. Thus, their assignments account for a large isotopic shift of the 297.1-cm⁻¹ band relative to those of the other two bands. The band at 677.8 cm⁻¹ was assigned to the out-of-plane bending mode of the H₃CC(=O)C group by Mikami, *et al.*, and to a C–CH₃ bending coupled with a Pd–O stretching mode by Nakamoto, *et al.* In this case, the latter assignment seems to be more favorable.

Cu(acac)₂. From the infrared spectra (Figure 1) and the observed spectral data (Table IV), it can be seen that only two bands at 455.0 (B_{1u}) and 290.5 (B_{2u}) cm⁻¹ of ⁶³Cu(acac)₂ show relatively large isotopic shifts, and that both calculations^{3b,8} agree in assigning them to pure Cu–O stretching modes. Different band assignments have been proposed, however, for the vibrations (the 614.8- and 218.5-cm⁻¹ bands of ⁶³Cu(acac)₂) which give small isotopic shifts. Because of the reason mentioned earlier, no further discussions are possible at this time.

It should be noted from Figure 1 that the spectra of Pd(acac)₂ and Cu(acac)₂ are markedly different although both compounds have the same square-planar

Table IV. Observed Frequencies, Band Assignments, and Isotopic Shifts for Cu(acac)₂ (cm⁻¹)

Nakamoto, <i>et al.</i> ^{3b}	Mikami, <i>et al.</i> ⁸	Present work	
		⁶³ Cu	Shift ^a
781, π(CH)	780, π(CH)	780.0	0.0
684, ring + ν(CuO)	684, ν(CR) + ring + ν(CuO)	685.0	0.1
654, δ(CR) + ν(CuO)	653, π(RCCO)	653.8	0.0
614, π ?	612, ring + ν(CuO)	614.8	0.2
455, ν(Cu)	451, ν(CuO)	455.0	1.0
427, ?	431, ring	432.2	0.0
(373), ring			
(302), ν(CuO)	291, ν(CuO)	290.5	3.5
(272), δ(CR)	268, δ(CR) + ν(CuO)	264.0	0.0
	217, π(ring)	218.5	0.3
(197), ring	187, ring	177.0	0.0
	167, π(ring)	170.0	0.0
	108, τ(R)	104.0	0.0

^a $\bar{\nu}({}^{63}\text{Cu}) - \bar{\nu}({}^{65}\text{Cu})$.

structure. This difference can be accounted for by considering the results of normal coordinate analyses on both compounds. According to Mikami, *et al.*,⁸ the 263-cm⁻¹ band of Pd(acac)₂ is an overlap of two bands; a ring deformation (B_{1u}) and a Pd-O stretching coupled with a C-CH₃ bending (B_{3u}). In the case of Cu(acac)₂, the latter band is shifted to 217 cm⁻¹ mainly because the Cu-O stretching force constant (1.45 mdyn/Å) is smaller than the Pd-O stretching force constant (1.85 mdyn/Å).

trans-Ni(acac)₂(pyridine)₂ and [Ni(acac)₂]₃. *trans*-Ni(acac)₂(pyridine)₂ is monomeric octahedral whereas Ni(acac)₂ is trimeric octahedral.¹¹ It is, therefore, of particular interest to compare the Ni-O stretching vibrations of these two types of complexes. The spectra, the observed frequencies, and isotopic shifts for these compounds are shown in Figure 1 and Table V. The

Table V. Observed Frequencies, Band Assignments, and Isotopic Shifts for *trans*-Ni(acac)₂(pyridine)₂ and [Ni(acac)₂]₃ (cm⁻¹)

—Ni(acac) ₂ (pyridine) ₂ —			[Ni(acac) ₂] ₃		Assignment
Nakamoto, <i>et al.</i> ^c	⁵⁸ Ni	Δ ^{pb}	⁵⁸ Ni	Δ ^{pb}	
766	766.0	0.0	755.0	0.0	π(CH)
654	654.0	-0.2	651.8	0.3	ν(CR) + ring + ν(NiO)
630	631.3	0.5	<i>a</i>		π(RCCO)
572	574.6	0.8	570.0	0.2	ring + ν(NiO)
439	438.0	0.8	421.1	0.6	ν(NiO) + ν(CR)
419	418.2	0.4	<i>a</i>		Ring
(373)	<i>a</i>		340.1	0.0	Ring
(276)	270.8	5.4	228.6	2.6	ν(NiO)
(253)	<i>a</i>		<i>a</i>		δ(CR)
	249.3	3.8			ν(Ni-pyridine)
(182)			190.5	0.0	Ring

^a Overlapped by neighboring band. ^b $\bar{\nu}({}^{58}\text{Ni}) - \bar{\nu}({}^{62}\text{Ni})$. ^c K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 4533 (1961).

(11) G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961); *Inorg. Chem.*, **4**, 456 (1965).

former compound exhibits two bands at *ca.* 271 and 249 cm⁻¹ which show isotopic shifts of more than 3.8 cm⁻¹. The latter band is probably due to the Ni-pyridine stretching mode since the same modes are assigned at 240–210 cm⁻¹ in octahedral Ni(II) pyridine complexes.¹² The 271-cm⁻¹ band is assigned to a pure Ni-O stretching mode of the monomeric species.

The spectrum of the trimeric complex is surprisingly simple in view of its complex structure; it shows only three broad bands between 500 and 200 cm⁻¹. This may be due to the relatively high symmetry of the trimeric structure and to an overlap of bands of similar nature which absorb at similar frequencies. As is seen in Table V, only two bands at 421.1 and 228.6 cm⁻¹ of the ⁵⁸Ni complex give isotopic shifts of more than 0.5 cm⁻¹ by the ⁵⁸Ni-⁶²Ni substitution. The 228.6-cm⁻¹ band is due to a purer Ni-O stretching mode than the 421.1-cm⁻¹ band since the former gives a larger isotope shift (2.6 cm⁻¹) than the latter (0.6 cm⁻¹). Table V lists empirical band assignments which are based on the results obtained by Mikami, *et al.*,⁸ for other acetylacetonato complexes.

Comments on Normal Coordinate Analysis. Several investigators^{6,7} have questioned the validity of the band assignments obtained from normal coordinate analysis on complex molecules such as metal acetylacetonates especially when the Urey-Bradley potential field was employed. The present metal isotope studies show, however, that these theoretical band assignments are essentially correct although some discrepancies are observed because of the 1:1 model approximation used.^{2,3} Some minor discrepancies between theoretical assignments and observed metal isotope shifts have been noted for ligand or ring vibrations in which the M-O stretching modes are partially involved. In order to refine the calculations, it is necessary to carry out rigorous treatments on a pair of isotopic molecules and to obtain good agreement between theoretical and observed isotopic shifts. Such calculations are, however, beyond the scope of our present study.

(12) R. J. H. Clark and C. S. Williams, *ibid.*, **4**, 350 (1965).