Binary Transition Metal Dinitrogen Complexes. III. Metal–Nitrogen Stretching Modes of $Ni(N_2)_n$, $Pd(N_2)_m$, and $Pt(N_2)_m$ (where n = 1–4 and m = 1–3)

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Abstract: Low frequency vibrations have been observed for $Ni(N_2)_n$, $Pd(N_2)_m$, and $Pt(N_2)_m$ (where n = 1–4 and m = 1–3) and are assigned to metal–nitrogen stretching modes and, moreover, the bis(dinitrogen) platinum controversy is reconciled. Data from detailed nitrogen isotopic substitution, together with these low frequency modes, make possible the calculation of accurate force constants for the monodinitrogen complexes. MVFF calculations are performed on the less complete data of the bis(dinitrogen) complexes and only simple point mass calculations are possible for the tris- and tetrakis(dinitrogen) complexes. Trends in the values of the mono(dinitrogen) force constants are discussed in terms of the nature of the $M-N_2$ interaction.

The first complex to be discovered with dinitrogen directly attached as a ligand was $[Ru(NH_3)_5N_2]^{2+}$.[1] Since then many new types of dinitrogen complexes have been synthesized by chemists, often with the ultimate aim of simulating in the laboratory reaction conditions whereby molecular dinitrogen can be converted to ammonia, hoping thereby to gain an insight into the biological fixation of molecular dinitrogen.

A characteristic feature of a dinitrogen complex is the NN stretching vibration. The frequencies and intensities of these modes have been related to a host of molecular properties such as σ and π overlap populations,[2] the synergic bonding mechanism, NN bond force constants and indirectly MN bond strengths,[3,4] thermodynamic stabilities,[5] the nature of chemisorbed N_2,[6] to name but a few. Although the similarities and differences between N_2 and CO coordinated to transition metals has been well demonstrated,[7] the nature of the $M-N_2$ interaction is not very well understood. Moreover, definitive $M-N_2$ frequencies only exist for the dinitrogen pentaammine complexes of ruthenium and osmium.[8] It is difficult to explain the scarcity of $M-N_2$ vibrational data, although it could relate to the low absorbance of these modes and/or the difficulty of distinguishing $\nu(M-N_2)$ modes from other low frequency modes in a region of the spectrum which is difficult to assign.

Recently a number of binary dinitrogen complexes have been synthesized under cryogenic conditions using metal atom cocondensation techniques. The complexes have all been of the type $M(N_2)_n$ where M includes Ni,[4] Pd,[4] Pt,[5,9] Co,[10] and Rh.[11] A feature common to most of these complexes was the difficulty of observing $M-N_2$ stretching modes owing to their low absorbances, a problem which could be surmounted by using long matrix depositions. In this paper we report and discuss the low frequency data for the binary dinitrogen complexes of Ni, Pd, and Pt.

Experimental Section

Monatomic Ni and Pd vapors were generated by directly heating a thin (0.008 in.) ribbon filament of the metal with ac, and monatomic Pt vapor by directly heating a Pt wire (0.01 in.) wound around a tungsten rod (0.06 in.). The nickel (99.99%), palladium (99.99%), and platinum (99.99%) were supplied by McKay Inc., N.Y. Research grade $^{14}N_2$ (99.99%) and Ar (99.99%) were supplied by Matheson. Isotopically enriched $^{15}N_2$ (99.5%) was supplied by Prochem. A mixture of $^{14}N_2$, $^{15}N^{14}N$, and $^{15}N_2$ in the ratio 1:2:1 was prepared by the technique described previously.[5]

The furnace used for the evaporation of the metals has been described previously.[12] The rate of metal atom depositions was continuously monitored using a quartz crystal microbalance.[13] The deposition rate was set such that the probability that a metal atom had another metal atom as a nearest neighbor in either the N_2 or Ar fccub lattice was approximately 1 in 10^3. Matrix gas flows, controlled by a calibrated micrometer needle valve, were usually in the range 2–8 mmol/hr. In the infrared experiments matrices were deposited on a cryotip cooled to 12–15°K by means of an Air Products Displex closed cycle helium refrigerator or a liquid helium transfer system cooled to 6.0–8.0°K. Spectra were recorded on Perkin-Elmer 180 and 621 spectrophotometers.

Results and Discussion

Metal–Ligand Stretching Modes. When the infrared active NN stretching modes for the complexes $M(N_2)_n$ were arranged to be strongly absorbing, it was relatively easy to observe weak absorptions in the region below 500 cm^{-1}. Warm-up experiments demonstrated that only one low frequency mode could be associated with each of the complexes M = Ni (n = 1–4) or M = Pd or Pt (n = 1–3).

Unfortunately, there exist very little literature data which are helpful in the assignment of these low frequency modes. Probably the most useful sources of information are the binary carbonyls and the nitrogen isotope studies[8] of $Ru(NH_3)_5({}^nN^mN)^{2+}$ (where n,m = 14 or 15). For example, $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ show low frequency M–C stretching and $\delta(M\hat{C}O)$ and $\delta(MC)$ deformational modes.[14] The $\delta(MC)$ modes occur at very low frequencies, below 100 cm^{-1}, making it unlikely that the analogous mode for $M(N_2)_n$ would be observed in our spectrometer range, 4000–200 cm^{-1}. It therefore remains to assign the low frequency mode to either a $\nu(M-N_2)$ or a $\delta(M-\hat{N}-N)$ vibration. Again, the analogy with binary carbonyls is useful, as the $\delta(M-\hat{C}-O)$ vibrations invariably occur to higher frequencies than the $\nu(M-C)$ vibrations, the latter being by far the more intense.[15] Similarly, the degenerate bending frequency $\delta(Ru-\hat{N}-N)$ in $Ru(NH_3)_5({}^{14}N_2)^{2+}$ has been convincingly assigned at about 508 cm^{-1} (for about every salt) and in all cases at a substantially higher frequency than the corresponding $\nu(RuN_2)$ stretching mode observed at about 446 cm^{-1}.[8] Furthermore, it is noteworthy that $Rh(N_2)_4$ shows very weak absorptions at 532/543 cm^{-1} together with a stronger absorption at 345 cm^{-1}.[11] By analogy with $Ni(CO)_4$ these lines were assigned to the $\delta(Rh-\hat{N}-N)$ and $\nu(Rh-N_2)$, respectively.[11]

It thus seems reasonable to deduce that the low frequency infrared active modes observed for $M(N_2)_n$ (Table I) are the $\nu(M-N_2)$ stretching modes and it is on this assumption that we will proceed to discuss the frequency and force constant trends and the nature of the $M-N_2$ interaction.

Table I. Nitrogen and Metal–Nitrogen Stretching Modes[a] for $Ni(N_2)_n$, $Pd(N_2)_m$, and $Pt(N_2)_m$ (where n = 1–4, m = 1–3)

	ν(NN)	ν(MN)
	$Ni(N_2)_n$	
n = 1	2089.9	466
2	2106.0	406
3	2134.0	343
4	2175.0	282
	$Pd(N_2)_m$	
m = 1	2213.0	378
2	2234.0	339 (330)
3	2242.0	350
	$Pt(N_2)_m$	
m = 1	2170.0	394 (388)
2	2197.5	360
3	2211.5	390

[a] Frequencies in parentheses represent the observed mode using $^{15}N_2$ isotopic substitution. All frequencies are in cm^{-1}.

We have shown previously that the Cotton-Kraihanzel force field approximation, applied usually to CO in carbonyls, is equally successful in predicting NN stretching frequencies and intensities for N_2 in binary dinitrogen complexes.[4] However, in this particular study we are interested primarily in gaining a direct insight into the $M-N_2$ bond and obviously a different approach is necessary.

Only in the case of the mono(dinitrogen) complexes do we have a sufficiently complete set of isotopic data to merit an exact force field calculation. Partial vibrational data are available for the bis(dinitrogen) complexes, so only a modified valence force field (MVFF) calculation was deemed worthwhile. In the case of the tris- and tetrakis(dinitrogen) complexes, there are clearly insufficient data to permit a normal coordinate calculation. We have, however, noted previously[5] that a full analysis of $Ni(^{12}C^{16}O)_4$ yielded potential energy distributions which indicated that there was very little coupling between the ν(NiC) and $\delta(Ni-\hat{C}-O)$ modes.[15] Therefore a reasonable estimate of the $M-N_2$ bond stretching force constant for $M(N_2)_3$ and $M(N_2)_4$ may be obtained using a simple analysis in which N_2 is treated as a point mass of 28 au and

$$\lambda = (\mu_{N_2} + {}^3/_2\mu_M)(k_{MN} - k_{MN\cdot MN})$$

for $M(N_2)_3$ or

$$\lambda = (\mu_{N_2} + {}^4/_3\mu_M)(k_{MN} - k_{MN\cdot MN})$$

for $M(N_2)_4$ where μ_{N_2} and μ_M are the reciprocal masses of N_2 and M, respectively, k_{MN} and $k_{MN\text{-}MN}$ are the stretch and stretch-stretch force constants, and $\lambda = 0.58915(\nu/1000)^2$ where ν is the $M-N_2$ stretching frequency.

Mono(dinitrogen) Complexes, MN_2. The four isotopic NN stretching frequencies of Ni^nN^mN (where n,m = 14 or 15) have been observed[6a] and were incorporated into an iterative program for the direct calculation of the best fit k_{NiN}, k_{NN}, and $k_{NiN\cdot NN}$ force constants. However, because at the time the low mode had not been observed and because of the linear dependence of the four secular equations for the various permutations of ^{14}N and ^{15}N, the least-squares analysis allowed a relatively large spread of errors in the force constants, without significant changes in the computed frequency fits.[6a] Therefore, to obtain a more precise force field it is essential to have a knowledge of the M–N stretching mode. Although we have previously reported the $Ni^nN^mN^{4,6}$ and $Pt^nN^mN^5$ nitrogen isotopic data and observed the $^{14}N^{15}N$ isotopic split, the data described below for Pd^nN^mN are new.[17]

In a typical experiment, Pd atoms were cocondensed with $^{14}N_2$:$^{14}N^{15}N$:$^{15}N_2$:Ar ≃ 1:2:1:2000 isotopic mixtures, and the infrared spectrum shown in Figure 1 was obtained. The isotope pattern is quite characteristic of a mono(dinitrogen) complex,[6a] where the original $Pd^{14}N_2$ absorption can be seen to have experienced what is probably best described as a multiple trapping site effect at 2215/2211 cm^{-1}. The corresponding $Pd^{15}N_2$ doublet is observed at 2140.7/2136.7 cm^{-1}. However, each component of this matrix split doublet produces a corresponding line of approximately equal intensity in the $^{14}N^{15}N$ region, which are themselves split by 0.8 cm^{-1} and thereby provide unequivocal evidence that the dinitrogen ligand in PdN_2 (in both sites) is bonded in an end-on fashion to the palladium.

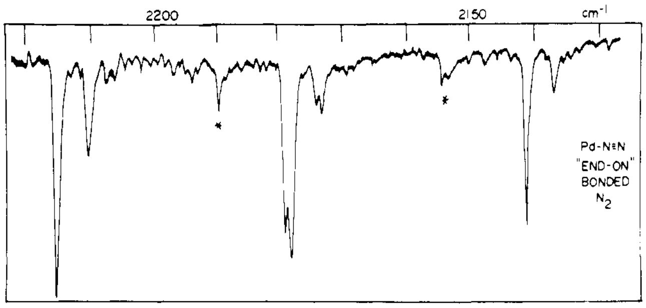


Figure 1. Infrared spectrum of Pd^nN^mN (where n, m = 14 or 15) resulting from the cocondensation of Pd atoms with $^{14}N_2$:$^{14}N^{15}N$:$^{15}N_2$:Ar = 1:2:1:2000 mixtures at 10°K showing the NN stretching region (the asterisk represents a trace quantity of the bis(dinitrogen) complex).

Table II lists the four isotopic NN stretching frequencies and the M–N stretching frequencies for NiN_2, PdN_2, and PtN_2. The metal-nitrogen and nitrogen-nitrogen stretching force constants as well as the stretch-stretch interaction force constants, compatible with the MVFF approximation, were derived assuming MN_2 to be a linear triatomic molecule. A least-squares analysis of the data was carried out to obtain values of k_{NN}, k_{MN}, and $k_{MN\cdot NN}$ which gave the best fit between observed and calculated frequencies. The calculated frequencies are listed in Table II and are found to be in excellent agreement with the observed. The best fit force constants are also shown in Table II.

Bis(dinitrogen) Complexes, $M(N_2)_2$. The NN stretching frequencies for $Ni(N_2)_2$ and $Pd(N_2)_2$ have been reported by Kündig et al.[4] who also investigated $Pt(N_2)_2$.[5] In this context a discrepancy that presently exists in the literature deserves clarification. Gruen and Green[9] independently reported infrared spectroscopic data for $Pt(N_2)_2$ obtained by cocondensing Pt atoms, formed in a hollow cathode sputtering device, with N_2–Ar matrices.

Although there was general agreement between the data for $Pt(N_2)$, there was general disagreement for the $Pt(N_2)_2$ complex. Both groups had clear evidence from nitrogen isotope studies for a bis(dinitrogen) species. However, Kündig's absorbed at 2150 cm^{-1} and Gruen's at 2197.6 cm^{-1}. In the light of monotonic trends in the function $\Delta H_c = n\Delta F_{NN}{}^5$ for the $Ni(N_2)_n$ and $Pd(N_2)_n$ complexes, Gruen's assignment would appear to be correct (Figure 2). To establish which is the authentic $Pt(N_2)_2$ complex, we have reinvestigated the $Pt-N_2-Ar$ cocondensation reaction at low Pt concentrations and have now obtained infrared data for $Pt(^{14}N_2)_n(^{15}N_2)_{2-n}$ (where n = 0–2) which are essentially identical with those of Gruen in terms of the frequencies and intensities of the observed isotopic lines. Furthermore, we have now observed the asymmetric ν(Pt–N) stretching mode at 360 cm^{-1}.

It is perhaps worth commenting that the rates of Pt atom deposition in Kündig's original experiments[5] were of the same order as those used in the original $Ni(N_2)_n$ and $Pd(N_2)_m$ experiments,[4] which have been confirmed in this study and yield only mononuclear complexes. As Pt atoms might be anticipated to have less tendency to dimerize or aggregate under matrix cocondensation conditions than Ni

Table II. Observed and Calculated Frequencies[a] and Force Constants[b] for Linear M^nN^mN (where M = Ni, Pd, or Pt; *m*, *n* = 14, 15)

NiN_2		PdN_2		PtN_2		
Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Assignment
2019.8	2020.6	2139.4	2138.7	2099.5	2100.5	$M^{15}N_2$
2053.5	2053.6	2176.9	2178.0	2134.7	2134.5	$M^{14}N^{15}N$
2057.6	2057.4	2177.7	2178.8	2138.7	2138.5	$M^{15}N^{14}N$
2090.7	2089.0	2214.5	2213.0	2173.2	2172.8	$M^{14}N_2$
466.0	466.0	377.8	378.0	393.9	394	$\nu(MN)$
2.48		1.86		2.29		k_{MN}
17.62		20.46		19.00		k_{NN}
0.25		0.72		0.12		$k_{MN \cdot NN}$

[a] Frequencies are in cm^{-1}. [b] Force constants are in mdyn/Å.

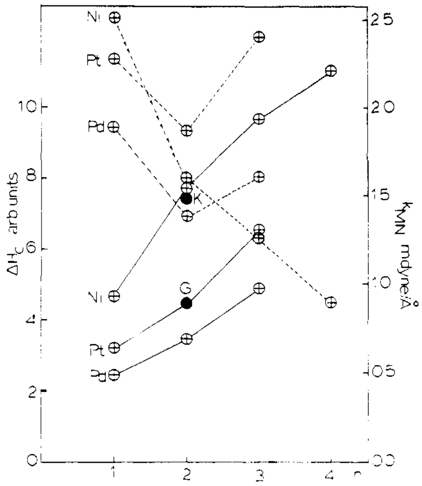
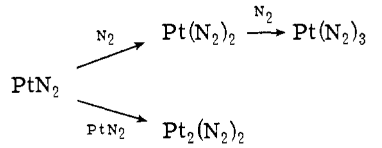
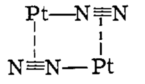


Figure 2. Graphical illustration of ΔH_c and k_{MN} vs. *n* for the complexes $M(N_2)_n$. (G = Gruen's bis(dinitrogen) data,[9] K = Kündig's bis(dinitrogen) data.[5] The solid line refers to ΔH_c and the dashed line to k_{MN}.)

or Pd atoms,[18] we find it difficult to believe that Kündig's bis(dinitrogen) complex formed from Pt_2 in the surface regions of the matrix during deposition. It is conceivable, however, that the mono(dinitrogen) complex undergoes rapid matrix dimerization during warm-up



to form $Pt_2(N_2)_2$ which is then essentially inert to further reaction with N_2. If Kündig's bis(dinitrogen) complex is in fact $Pt_2(N_2)_2$, then the unusually high activation energy which was observed to separate the bis(dinitrogen) complex from $Pt(N_2)_3$ becomes understandable.[5] Moreover, the observed shift to frequencies lower than any of the mononuclear $Pt(N_2)_n$ complexes[5] would imply some kind of bridging N_2 interaction in $Pt_2(N_2)_2$, for example



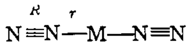
as the effect of metal aggregation on terminally bonded ligands is to shift the frequencies to considerably higher values than those observed for the corresponding mononuclear complexes.[18]

At this stage, these discussions can only be considered as speculative. Confirmation must await the results of detailed Pt concentration experiments.

Table III. Calculated and Observed Frequencies for the Isotopically Labeled Bis(dinitrogen) Complexes of Ni, Pd, and Pt

Molecule	Mode assignment	Obsd (cm^{-1})	Calcd (cm^{-1})
$Ni(^{14}N_2)_2$	ν(N–N)sym	2187	2187.5
	ν(N–N)asym	2106	2106.2
	ν(M–N)sym		328.4
	ν(M–N)asym	406	405.5
$Ni(^{15}N_2)_2$	ν(N–N)sym		2113.4
	ν(N–N)asym	2036	2034.8
	ν(M–N)sym		317.3
	ν(M–N)asym		398.6
$Ni(^{14}N_2)(^{15}N_2)$	$\nu(^{14}N–^{14}N)$	2166	2164.5
	$\nu(^{15}N–^{15}N)$	2056	2056.4
	ν(M–N)		322.7
	ν(M–N)		402.3
$Ni(^{14}N^{15}N)_2$	$\nu(^{14}N–^{15}N)$sym		2152.0
	$\nu(^{14}N–^{15}N)$asym		2071.8
$Ni(^{15}N^{14}N)_2$	$\nu(^{15}N–^{14}N)$sym		2149.6
	$\nu(^{15}N–^{14}N)$asym		2069.9
$Pd(^{14}N_2)_2$	ν(N–N)sym	2267.0	2266.8
	ν(N–N)asym	2234.0	2235.0
	ν(M–N)sym		303.6
	ν(M–N)asym	339	338.8
$Pd(^{15}N_2)_2$	ν(N–N)sym		2189.9
	ν(N–N)asym	2159.5	2159.2
	ν(M–N)sym		293.3
	ν(M–N)asym	330	331.3
$Pd(^{14}N_2)(^{15}N_2)$	$\nu(^{14}N–^{14}N)$	2252.2	2253.5
	$\nu(^{15}N–^{15}N)$	2171.5	2171.0
	ν(M–N)		306.9
	ν(M–N)		333.3
$Pd(^{14}N^{15}N)_2$	$\nu(^{14}N–^{15}N)$		2228.7
	$\nu(^{14}N–^{15}N)$		2197.3
$Pd(^{15}N^{14}N)_2$	$\nu(^{15}N–^{14}N)$		2228.7
	$\nu(^{15}N–^{14}N)$		2197.6
$Pt(^{14}N_2)_2$	ν(N–N)sym		2249.2
	ν(N–N)asym	2197.5	2198.3
	ν(M–N)sym		349.6
	ν(M–N)asym	360	359.7
$Pt(^{15}N_2)_2$	ν(N–N)sym		2173.0
	ν(N–N)asym	2125.0	2123.8
	ν(M–N)sym		337.8
	ν(M–N)asym		350.2
$Pt(^{14}N_2)(^{15}N_2)$	$\nu(^{14}N–^{14}N)$	2231.0	2231.3
	$\nu(^{15}N–^{15}N)$	2140.0	2140.8
	ν(M–N)		341.6
	ν(M–N)		357.1
$Pt(^{14}N^{15}N)_2$	$\nu(^{14}N–^{15}N)$sym		2213.2
	$\nu(^{14}N–^{15}N)$asym		2162.8
$Pt(^{15}N^{14}N)_2$	$\nu(^{15}N–^{14}N)$sym		2209.8
	$\nu(^{15}N–^{14}N)$asym		2160.0

MVFF Calculations for $M(N_2)_2$ (where M = Ni, Pd, or Pt). In the case of $M(N_2)_2$, four infrared active isotopic NN stretching modes are available together with the asymmetric MN stretching mode. The Raman active NN stretching mode is available for $Ni(N_2)_2$ and $Pd(N_2)_2$.[4] Assuming a linear bis(dinitrogen) complex



$$\overset{R}{N{\equiv}N}\overset{r}{—}M—N{\equiv}N$$

a least-squares analysis of the data was performed by adjusting the values of the four parameters k_r, k_R, k_{rR}, and k_{RR}, with k_{rr} fixed at 10% of k_r. The calculated and ob-

Table IV. Best Fit MVFF Force Constants[a] for the Bis(dinitrogen) Complexes of Nickel, Palladium, and Platinum

	$Ni(N_2)_2$	$Pd(N_2)_2$	$Pt(N_2)_2$
k_R	18.85	21.26	20.03
k_r	1.60	1.38	1.87
k_{RR}	0.68	0.27	0.43
k_{rr}	0.20	0.14	0.19
k_{rR}	0.25	0.72	0.12

[a] In mdyn/Å.

served frequencies are listed in Tables III and are found to be in excellent agreement for all lines. In Table IV the respective best fit force constants are listed.

Tris(dinitrogen) Complexes, $M(N_2)_3$. Using the point mass approximation referred to earlier and the observed asymmetric M-N stretching modes for triangular planar $M(N_2)_3$ (where M = Ni, Pd, or Pt),[4,5] one can calculate values for the F matrix terms $k_{MN} - k_{MN \cdot MN}$. As the totally symmetric M-N stretching modes have not been observed, one can only guess values for the stretch-stretch interaction constant $k_{MN \cdot MN}$. For $k_{MN \cdot MN} = 0.1 k_{MN}$ (an approximation commonly used), the values for k_{MN} listed in Table V are obtained. The reported k_{NN} force constants[4,5] are those values resulting from the application of the Cotton-Kraihanzel approximation to the observed infrared and Raman active asymmetric and symmetric ν(NN) stretching modes and should of course be quite accurate (C.K. values appear to differ only by about 2% from the MVFF values as seen from the $M(N_2)$ and $M(N_2)_2$ calculations, Table V).

Discussion of Results. The computed values of k_{MN} for the complexes $M(N_2)_n$ as a function of n are collected together in Table V and illustrated graphically in Figure 2. Aside from $Ni(N_2)_4$ for which there is as yet no palladium or platinum analog, the k_{MN} values appear to lie within the range 1.40-2.50 mdyn/Å. Of considerable interest is the observation that the ΔH_c function increases monotonically with n (Figure 2), retaining the order Ni > Pt > Pd, whereas the k_{MN} values are amonotonic for $Pd(N_2)_n$ and $Pt(N_2)_n$, with the orders juxtaposed as M and n vary.

If k_{MN} is any sort of measure of the metal-nitrogen bond strength and/or thermodynamic stability of the complex, then it would appear that, although ΔH_c is a parameter that appears to parallel the warm-up behavior of the complexes, it may not reflect the stability of the complex as measured by k_{MN}. Proof of this point will have to await more complete vibrational data for the bis- and tris(dinitrogen) complexes.

As the force constant calculations for the mono(dinitrogen) complexes are more reliable than those for the bis- and tris(dinitrogen) complexes, the following comments are probably justified. In terms of the nature of the $M-N_2$ interaction, it is significant that for MN_2 $k_{MN}{}^{Ni} > k_{MN}{}^{Pt} > k_{MN}{}^{Pd}$, an order which parallels in an inverse fashion the NN bond stretching force constants, $k_{NN}{}^{Pd} > k_{NN}{}^{Pt} > k_{NN}{}^{Ni}$. These trends are reminiscent of those observed in, for example, the tetracarbonyls of the same metals, thereby demonstrating the similarity in the bonding characteristics of N_2 and CO. The reversal in the order on going from $Pd(N_2)$ to $Pt(N_2)$ could be a manifestation of the lanthanide contraction.

Table V. Summary of NN and MN Force Constants for $Ni(N_2)_n$, $Pd(N_2)_m$, and $Pt(N_2)_m$ (where n = 1-4 and m = 1-3)

	k_{NN}[c]	k_{MN}
	$Ni(N_2)_n$	
n = 1	17.62 (17.97)	2.51
2	18.85 (18.76)	1.60
3	19.38[b]	1.26[a]
4	19.85[b]	0.90[a]
	$Pd(N_2)_m$	
m = 1	20.47 (20.19)	1.89
2	21.26 (20.87)	1.38
3	20.97[b]	1.61[a]
	$Pt(N_2)_m$	
m = 1	19.00 (19.44)	2.27
2	20.03 (20.38)	1.87
3	20.43[b]	2.40[a]

[a] Calculated using point mass model and $k_{MN \cdot MN} = 0.1 k_{MN}$. [b] Cotton-Kraihanzel value using observed infrared and Raman frequencies. [c] Cotton-Kraihanzel values (for comparison purposes) are shown in parentheses.

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