Binary compounds of Dinitrogen with Nickel, Chromium, Platinum, and Copper: A Vibrational Investigation of the Metal–Dinitrogen Linkage

By **J. K. Burdett, M. A. Graham,** and **J. J. Turner,***† University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The species NiN_2, CrN_2, and PtN_2 have been identified by i.r. spectroscopy in low-temperature matrices. The i.r. spectra of dinitrogen chemisorbed on metal clusters of copper, chromium, and nickel have also been obtained, the former for the first time. The bands due to NiN_2 and CrN_2 are split in the nitrogen matrix due to the presence of different sites.

It is suggested that the reason for the lack of observation of dinitrogen complexes beyond the bis-adduct is the deficiency of charge on the metal when dinitrogen binds as a ligand in an imperfectly synergistic process.

UNTIL lately the only metal dinitrogen compounds available for study contained other ligands bound to the central metal atom.[1] However, in this laboratory, we have recently obtained i.r. spectral evidence for binary nickel dinitrogen compounds by co-condensation of nickel atoms with dinitrogen at 20 K.[2] Using a low metal-atom concentration two sharp i.r. bands were observed in a pure N_2 matrix. Using a matrix of argon containing *ca.* 20% dinitrogen we were also able to see an i.r. absorption corresponding to dinitrogen adsorbed on a nickel atom cluster ($Ni_{cl}N_2$). The use of the matrix isolation technique in the study of adsorbed species has been discussed by us [2] and by Blyholder *et al.*[3]

In the work reported here we have extended this technique to other metals, chromium, platinum, and copper, in order to examine some aspects of the bond existing between metal and dinitrogen. Although this exhibits some similarities to the metal–carbon bond in carbonyl complexes there are also some very interesting differences.

Chromium forms a stable hexacarbonyl at room temperature and the lower carbonyls of chromium and its congeners, molybdenum and tungsten, have been isolated in low-temperature matrices in this laboratory.[4] Nickel forms a stable tetracarbonyl. $Ni(CO)_3$ has been made by the matrix photolysis of the $Ni(CO)_4$ parent,[5] while $Ni(CO)_{1-4}$ have been prepared [6] by cocondensation of nickel atoms in an argon/CO matrix at 4 K. Platinum forms only the ill-defined $(Pt(CO)_2)_n$ species, and no other binary carbonyl, although compounds of the type $PtCOL_y$ are known where the L are ligands other than CO. Copper forms no carbonyl or carbonyl complex [except $\{Cu(CO)Cl_2\}_2$] stable at room temperature, although i.r. evidence for a carbonyl of copper has been presented recently from co-condensation of copper atoms with carbon monoxide at low temperatures.[7] Recently $Pd(CO)_4$ [8] and $U(CO)_{1-6}$ [9] have been identified using similar techniques.

Mann and Broida [10] have investigated the u.v. spectra of transition-metal atoms in rare-gas matrices. They found that spectra of the isolated atoms could be obtained for chromium and nickel atoms (amongst others) in argon at 20 K but that attempts to study atomic copper at this temperature were unsuccessful. At 4 K atomic spectra could be obtained for copper and it is suggested that at 20 K under the conditions used, the copper exists as clusters.

EXPERIMENTAL

A schematic of the experimental arrangement is shown in Figure 1. Metal atoms are sprayed on to the cold central (KBr) window from A and matrix gas (nitrogen/argon mixture) from B. The central window is cooled to 20 K using an Air Products AC-2L cryotip with gaseous hydrogen. By pumping on the hydrogen a temperature of *ca.* 16 K can be obtained, as measured by a Chromel/

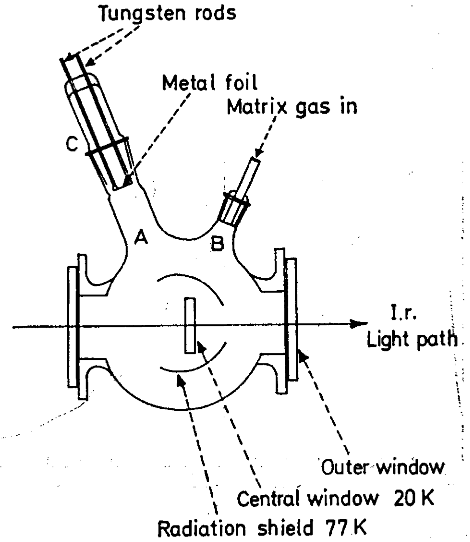

FIGURE 1 Schematic experimental arrangement

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† *Present address:* Department of Inorganic Chemistry, The University, Newcastle-upon-Tyne NE1 7RU.

[1] For example see A. D. Allen and F. Bottomley, *Accounts Chem. Research*, 1968, **1**, 360; Yu. G. Borod'ko and A. E. Shilov, *Russ. Chem. Rev.*, 1969, **38**, 355.

[2] J. K. Burdett and J. J. Turner, *Chem. Comm.*, 1971, 885.

[3] G. Blyholder, M. Tanaka, and J. D. Richardson, *Chem. Comm.*, 1971, 499.

[4] M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2939; M. A. Graham, A. J. Rest, and J. J. Turner, to be published; M. A. Graham, Ph.D. Thesis, University of Cambridge, 1971.

[5] A. J. Rest and J. J. Turner, *Chem. Comm.*, 1969, 1026.

[6] R. L. DeKock, *Inorg. Chem.*, 1971, **10**, 1205.

[7] J. S. Ogden, *Chem. Comm.*, 1971, 978.

[8] J. H. Darling and J. S. Ogden, *Inorg. Chem.*, 1972, **11**, 666.

[9] J. L. Slater, R. K. Sheline, and W. Weltner, jun., *J. Chem. Phys.*, 1971, **55**, 5129.

[10] D. M. Mann and H. P. Broida, *J. Chem. Phys.*, 1971, **55**, 84.

Constantan thermocouple embedded in the central window. The metal atom source C consists of an electrically heated foil of the metal under examination. Power is fed to the foil, which is typically a few thousands of a centimetre thick, by two 0·15 cm diameter tungsten rods *ca.* 3-cm long. The entire heater section is air cooled. The central window is rotated so that there is no direct line-of-sight from foil to window and the metal surface is cleaned in two heating steps. First, power is applied to the foil under vacuum and adsorbed gas removed by simple heating. Subsequently the top surface of the metal is removed by raising the foil temperature until a metal mirror may be seen on the glass round the heater. The pressure at this stage within the vacuum jacket is better than 10^{-6} Torr. The window is now rotated back into position facing ports A and B.

Nitrogen (gas) is sprayed on through orifice B and the foil temperature increased until i.r. absorptions are detected. We have no accurate method by which to determine the foil temperature and hence absolute matrix concentration of atoms. However a reasonable estimate may be obtained from published vapour-pressure data; for a convenient deposition vapour-pressure of *ca.* 10^{-6} mm, the appropriate metal temperatures are Cu[11] (910—1000 °C); Cr[12] (1070—1140 °C), Ni[13] (1140—1230 °C), and Pt[14] (1600—1720 °C).

The nickel foil was supplied by Wiggin and Co., and the copper and platinum by Johnson-Matthey. Chromium is unobtainable as foil or wire and two sample preparation techniques were employed. In the first chromium was evaporated under vacuum from pellet form (99·999% Cr) on to a thin platinum foil to produce a smooth surface. A more uniform film was produced electrolytically.[15] Nitrogen (gas) was supplied by BOC (Grade X $^{14}N_2$) and by Prochem Ltd., (99% $^{15}N_2$). I.r. spectra were recorded on a Perkin-Elmer 521 spectrometer which was regularly calibrated with DCl and had an accuracy of $\pm0·3$ cm^{-1} in the 2300—2000 cm^{-1} region.

RESULTS

Nickel.—As we have discussed previously[2] for nickel, two i.r. absorptions at 2179·8 and 2169·4 cm^{-1} were observed when a low atom flux of nickel was co-condensed with an excess of gaseous nitrogen. Using a matrix of pure $^{15}N_2$, these two bands shifted by *ca.* 73 cm^{-1} to lower frequency, *i.e.* 2106·2 and 2096·4, confirming that they are both NN stretching frequencies of one or more species. On using a mixture of $^{14}N_2$ and $^{15}N_2$ we observed (see Figure 2) a superposition of the bands (labelled A_1, A_2, B_1, B_2) seen in individual $^{14}N_2$ and $^{15}N_2$ experiments, but in addition two bands at 2177·2 (A_3) and 2108·2 (B_3) cm^{-1} were seen. It was suggested[2] that this behaviour was consistent with the formation of $Ni(N_2)$ and $Ni(N_2)_2$, the six bands of Figure 2 being assigned as NiN_2 (the two strong bands A_1B_1 which are unsplit on using a $^{14}N_2/^{15}N_2$ mixture) and $Ni(N_2)_2$ (the weaker bands A_2B_2, and the bands A_3B_3). However, this behaviour of the bands $Ni(N_2)_2$ on mixed isotopic substitution is very different from that of the corresponding carbonyls $M(CO)_2$.

On co-condensing Ni atoms with CO, bands due to Ni(CO), $Ni(CO)_2$, $Ni(CO)_3$, and $Ni(CO)_4$ have been assigned.[6] Since OCNiCO is linear in each of $^{16}OCNiC^{16}O$ and $^{18}OCNiC^{18}O$, there is one i.r. absorption due to the asymmetric CO stretching vibration. With a 1 : 1 $C^{16}O/C^{18}O$ mixture only *one* new band assignable as an $Ni(CO)_2$ species was observed. Moreover this band lay approximately halfway between the absorptions due to $^{16}OCNiC^{16}O$ and $^{18}OCNiC^{18}O$ and was about twice as intense as each of these latter two bands. This band may therefore be assigned to a pseudo asymmetric vibration of $^{16}OCNiC^{18}O$.

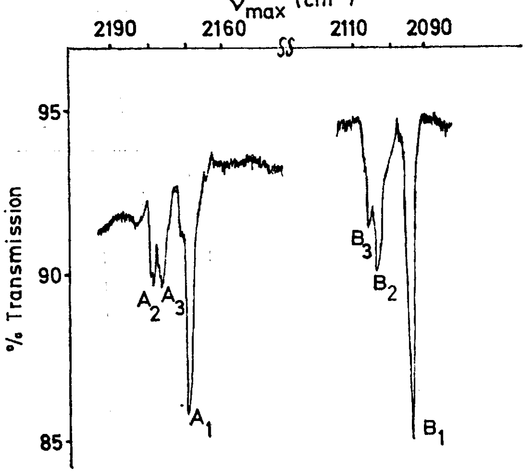

FIGURE 2 I.r. spectrum from co-condensation of nickel atoms with a 1 : 1 mixture of $^{14}N_2/^{15}N_2$. A_1A_2 = bands present using pure $^{14}N_2$, B_1B_2 = bands present using pure $^{15}N_2$, A_3B_3 = new bands produced using a mixture of $^{14}N_2$ and $^{15}N_2$

Other observations of relevance to the Ni/N_2 experiments are: (i) In an argon matrix at 20 K the CO stretching vibration of NiCO produces a single band but in a nitrogen matrix, this band is split into two with a separation of *ca.* 2·5 cm^{-1}: CrCO in N_2 also gives rise[4] to a doublet of separation 12 cm^{-1}.

(ii) Moore and Pimentel[16] noted a splitting of 5·7 cm^{-1} for the N–N stretching mode of CH_2N_2 in nitrogen matrices and rationalised the behaviour on the basis of three different sites in solid N_2 which can accommodate the diazomethane molecule.

(iii) Splitting of vibrational bands of carbonyl species in *pure* matrices is often removed on doping the pure matrix (*e.g.* doping argon with 10% nitrogen).[4,17]

(iv) On co-condensing Ni atoms with mixed $^{14}N_2$/argon matrices (N_2 : Ar = 1 : 1 to 100 : 1) only one band was observed at 2169 cm^{-1} (*i.e.* A_1) and although this band was in general broader than the corresponding band in a pure nitrogen matrix it was not sufficiently broad to have obscured any band A_2.

(v) With a high Ni spray-on rate and a nitrogen doped argon matrix, a band was observed at 2206 cm^{-1}; this band could also be observed when the nickel was deposited

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[11] J. W. Edwards, H. L. Johnston, and W. E. Ditmars, *J. Amer. Chem. Soc.*, 1953, **75**, 2467.

[12] R. Speiser, H. L. Johnston, and P. Blackburn, *J. Amer. Chem. Soc.*, 1950, **72**, 4142.

[13] H. L. Johnston and A. L. Marshall, *J. Amer. Chem. Soc.*, 1940, **62**, 1382.

[14] S. Dushman and J. M. Lafferty (eds.), 'Scientific Foundations of Vacuum Technique,' 1962, Wiley, New York.

[15] A. H. Sully, 'Metallurgy of the Rarer Metals—1, Chromium,' Butterworths, London, 1954, p. 156.

[16] C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, 1964, **40**, 342.

[17] M. Poliakoff, Ph.D. Thesis, University of Cambridge, 1972.

very quickly with a *pure* nitrogen matrix. Several workers have noted a strong band at 2202 cm^{-1} due to adsorbed nitrogen molecules (in the so called γ_3 state) on nickel atom clusters within a certain size range ($15 < d < 75$ Å).

(vi) Using intermediate deposition conditions bands were observed at 2188·3 and 2196·4 cm^{-1}. These bands could also be produced by photolysis (300 nm $< \lambda <$ 330 nm) of matrices containing only the species responsible for A_1 and A_2 (see Figure 3).

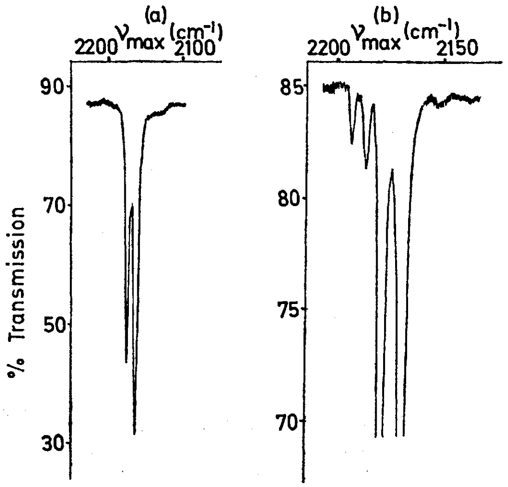

FIGURE 3 Behaviour on photolysis (300 nm $< \lambda <$ 330 nm) of nickel atoms, Ni/N_2 species in a $^{14}N_2$ matrix at 17 °K. (a) before photolysis, (b) after photolysis

(vii) In nitrogen matrices containing species A_1 and A_2 no change in the spectrum was observed on warming the matrix to *ca.* 35 K and recooling to 20 K.

The results seem consistent only with the following interpretation. (a) The bands A_1 and B_1 are due to $Ni^{14}N^{14}N$ and $Ni^{15}N^{15}N$ (probably not Ni_xN_2—see below) in sites in the matrix such that there is zero vibrational coupling with surrounding matrix molecules, *i.e.* the replacement of $^{14}N_2$ matrix molecules by either $^{15}N_2$ or argon does not affect the position of A_1 and similarly for B_1.

(b) The bands A_2 and B_2 are due to $Ni^{14}N^{14}N/^{14}N^{14}N$ and $Ni^{15}N^{15}N/^{15}N^{15}N$ respectively. Here we imply that there is vibrational coupling between say $Ni^{14}N^{14}N$ and another $^{14}N^{14}N$ molecule which is responsible for shifting the $^{14}N^{14}N$ stretch of $Ni^{14}N^{14}N$ from A_1 to A_2. On replacement of the coupled $^{14}N^{14}N$ by $^{15}N^{15}N$ the coupling is altered and the frequency shifts to A_3; similarly the $^{15}N^{15}N$ stretch of $Ni^{15}N^{15}N$ shifts to B_3 on replacing a coupled $^{15}N^{15}N$ by $^{14}N^{14}N$. On substantial altering of the molecular surroundings by doping the nitrogen matrix with argon the vibrational coupling is lost and $A_2A_3B_2B_3$ disappear. This implies that the species giving rise to $A_2A_3B_2B_3$ is *not* the molecule N_2NiN_2 with weak N_2/N_2 coupling (as previously suggested) since there is no reason why the $A_2A_3B_2B_3$ pattern should be removed on doping the nitrogen matrix with argon. It seems most probable that the species is $N{\equiv}N \cdots NiN_2$ or $NiN_2 \cdots N{\equiv}N$, *i.e.* NiN_2 coupled 'fore or aft' with a nitrogen molecule in the matrix. Moreover the weakly coupled NiN_2/N_2 system is more consistent with the lack of spectral change (vii) on slight annealing since this would have been expected to increase the amount of $Ni(N_2)_2$.

(c) The intensity pattern shown in Figure 2 matches the conclusions given in (a) and (b) as follows. The ratio $^{14}N_2 : {}^{15}N_2$ in the matrix gas is obtained from the intensity ratio $A_1(Ni^{14}N^{14}N) : B_1(Ni^{15}N^{15}N)$; if this has value x then the intensity ratio $A_2 : A_3 : B_3 : B_2$ is $x^2 : x : x : 1$. From Figure 2, $x = 0{\cdot}76$ which gives $A_2 : A_3 : B_3 : B_2 = 0{\cdot}58 : 0{\cdot}76 : 0{\cdot}76 : 1$; the experimentally observed intensity ratio was 0·59 : 0·67 : 0·71 : 1. With $^{14}N_2 : {}^{15}N_2 \equiv x = 3{\cdot}7$ (from intensity $A_1 : B_1$), $A_2 : A_3 : B_3 : B_2$ $(\equiv x^2 : x : x : 1)$ should be 13·8 : 3·7 : 3·7 : 1. However in this experiment B_2 was not resolved from B_3 so $A_2 : A_3 : (B_3 + B_2)$ should be 13·8 : 3·7 : 4·7 *i.e.* 3·7 : 1 : 1·3; observed ratios 3·1 : 1 : 1·6 which is reasonable given the experimental difficulty.

(d) The band at 2206 cm^{-1} is due to $Ni_{cl}N_2$ (*i.e.* a nitrogen molecule attached to a cluster of nickel atoms); the conditions necessary for the production of this band (v) are precisely those expected to produce excess nickel atoms and hence cluster formation. The bands produced under intermediate conditions (vi) are due to species such as $(Ni)_{2,3}N_2$. Thus we believe the bands $A_1A_2A_3B_1B_2B_3$ are all due to species containing one nickel atom. It is impossible to prove this completely since nickel has no convenient isotopes; even for the Li/N_2 compounds obtained by Andrews *et al*,[18] the ^6Li–^7Li isotope shifts were too small to come to any definite conclusion about the Li stoicheiometry.

Chromium.—In experiments with chromium atoms and dinitrogen strikingly similar results to those with nickel and dinitrogen were obtained. Figure 4(i) illustrates an experiment with chromium atoms and a 1 : 1 $^{14}N_2/^{15}N_2$ mixture; this can be directly compared with Figure 2 for nickel and the bands in Figure 4 have been labelled in the corresponding manner. Bands A_1 and B_1 are thus assigned to $Cr^{14}N^{14}N$ and $Cr^{15}N^{15}N$ unperturbed by the matrix nitrogen molecules, bands $A_2A_3B_2B_3$ to these molecules perturbed by a nitrogen molecule.

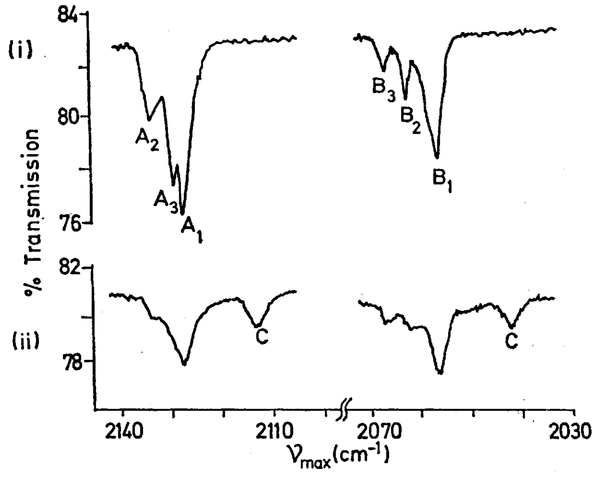

FIGURE 4 I.r. spectra from co-condensation of chromium atoms with a 1 : 1 mixture of $^{14}N_2/^{15}N_2$ (i) after spray on (ii) after 1 h photolysis $\lambda <$ 280 nm, $\lambda >$ 390 nm. A_1A_2 = bands present when only $^{14}N_2$ used, B_1B_2 = bands present using pure $^{15}N_2$, A_3B_3 = new bands produced using a mixture of $^{14}N_2$ and $^{15}N_2$, C = bands produced on photolysis

On photolysis of a $Cr/^{14}N_2$ sample with radiation $\lambda <$ 280,

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[18] R. C. Spiker, jun., L. Andrews, and C. Trindle, *J. Amer. Chem. Soc.*, 1972, **94**, 2401.

$\lambda > 390$ nm the intensity of the bands due to CrN_2 decreased, that due to the perturbed molecule (*i.e.* band A_2) disappearing first, and a new band appeared at 2112·8 cm^{-1}. With a pure $^{15}N_2$ matrix corresponding behaviour resulted in a band at 2042·1 cm^{-1}. On photolysis of a sample produced using a $^{14}N_2/^{15}N_2$ mixture these two bands appeared but no others—see Figure 4(ii). This indicates that the bands at 2042·1 and 2112·8 cm^{-1} result from a species containing a single dinitrogen unit. Prolonged photolysis led to the disappearance of these two bands and the appearance of new bands at 2089·8 ($^{14}N_2$) and 2020·0 ($^{15}N_2$) cm^{-1}. This behaviour is consistent with:

$$(\text{for } ^{14}N^{14}N)\underset{2126\cdot8\ \ 2133\cdot8}{\underset{A_1\quad A_2}{Cr^{14}N^{14}N}} \xrightarrow{h\nu} \underset{2112\cdot8}{(Cr)_x{}^{14}N^{14}N} \xrightarrow[h\nu]{\text{prolonged}} \underset{2089\cdot8}{Cr_{cl}{}^{14}N^{14}N}$$

This photolytic behaviour therefore matches that of nickel with the striking difference that the N–N stretch of $Ni_{cl}N_2$ is higher than that of NiN_2 but *vice versa* for chromium.

Platinum.—On spray on of platinum atoms with pure $^{14}N_2$ *or* $^{15}N_2$ i.r. absorptions were observed at 2205·6 cm^{-1} ($^{14}N_2$) or 2131·6 cm^{-1} ($^{15}N_2$), a $^{14}N_2/^{15}N_2$ shift of 74·0 cm^{-1}. Using a mixture of $^{14}N_2$ and $^{15}N_2$ no extra bands were seen neither did the breadth of the bands increase. Variations of the metal spray-on rate did not lead to any new absorptions. These experiments indicate the presence of only one dinitrogen attached to the platinum unit, leading to a formulation Pt_yN_2. The i.r. spectra of dinitrogen adsorbed on metal clusters of platinum and nickel have been observed by Van Hardeveld and Van Montfoot,[19] who find a band at 2230 cm^{-1} for $Pt_{cl}N_2$. This leads us to suggest that the i.r. absorption observed by us is due to PtN_2. This data implies an approximate 25 cm^{-1} difference between ν(NN) in PtN_2 and $Pt_{cl}N$ to be compared to the 35 cm^{-1} difference observed above between NiN_2 and $Ni_{cl}N_2$. We have not observed the doublet structure in the i.r. region of PtN_2 in a nitrogen matrix, noted for NiN_2 and CrN_2. This may be due to the larger size of Pt compared to Cr or Ni. However the i.r. absorptions of PtN_2 were broader (5—6 cm^{-1} half-width) compared to those of CrN_2 and NiN_2 (2 cm^{-1}).

Copper.—Co-condensation of copper atoms with pure $^{14}N_2$ *or* $^{15}N_2$ led to i.r. absorptions at 2272·2 cm^{-1} ($^{14}N_2$) or 2195 cm^{-1} ($^{15}N_2$) a $^{14}N_2/^{15}N_2$ isotope shift of 76·9 cm^{-1}, the largest displacement recorded to date for a metal dinitrogen species. [Nitrogen (gas) is calculated[21] to have a shift of 81 cm^{-1}]. This i.r. absorption was only obtained using a high concentration of copper atoms such that there was a heavy opaque mirror of copper deposited on the glass surrounding the foil. No new bands (other than those present in separate $^{14}N_2/^{15}N_2$ experiments) arose when a mixture of $^{14}N_2/^{15}N_2$ was used indicating the presence of one metal–dinitrogen linkage per molecule and hence the absorptions are assigned to $Cu_y{}^{14}N^{14}N$ and $Cu_y{}^{15}N^{15}N$.

Since there have been no i.r. studies of nitrogen on copper clusters by conventional techniques we cannot assign a value for *y*. However Mann and Broida[10] observed that it was not possible to obtain u.v. spectra of isolated copper *atoms* in an argon matrix at 20 K presumably due to aggregation. Together with the present observation that *no* i.r. bands could be obtained with copper spray on rates as low as the successful rates for Ni, Cr, and Pt, this suggests that y = cluster.

DISCUSSION

Spectral Features.—One interesting feature of our spectroscopic findings is the strong correlation between the magnitude of the $^{14}N_2/^{15}N_2$ isotope shift and the value of the NN stretching frequency. Using a simple harmonic oscillator picture the value of the NN stretching frequency using a Cotton–Kraihanzel Force Field[20] is given simply by

$$\nu_I = K(k/\mu_I)^{\frac{1}{2}} \qquad (1)$$

where K is a constant, k is the NN stretching force constant and μ_I the reduced mass of the N_2 unit. The $^{14}N_2/^{15}N_2$ isotope shift Δν is then given by

$$\Delta\nu = \nu_{14}[1 - (\mu_{14}/\mu_{15})^{\frac{1}{2}}] = 0{\cdot}035\nu_{14} \qquad (2)$$

The observed $^{14}N_2/^{15}N_2$ shifts for the series of species described here are shown in Figure 5 as a function of ν_{14}.[21] Also included are the isotope shifts for some other dinitrogen complexes made available by kind permission of Professor J. Chatt. The slope of the line is *ca.* 0·04 in reasonable agreement with theory. For the species described in this work and also for the $Ni(CO)_3N_2$ complex, matrix frequencies have been used and the error is *ca.* 0·3 cm^{-1} for the isotope shift. For the other species the error is somewhat larger since these spectra were obtained in solution with larger band widths.

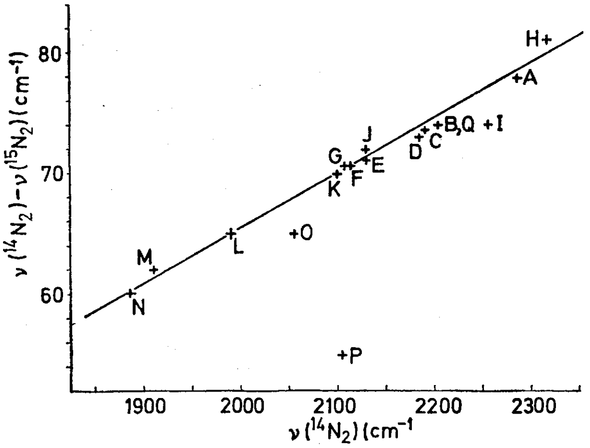

FIGURE 5 The $^{14}N_2/^{15}N_2$ isotope shift for a series of dinitrogen compounds. A = $Cu_{cl}N_2$; B = PtN_2; C = NiN_2/N_2; D = NiN_2; E = CrN_2/N_2; F = CrN_2; G = Cr_2N_2; H = N_2; I = $Ni(CO)_3N_2$; J = $Ru(NH_3)_5N_2I_2$; K = $[Ru(NH_3)_5N_2]_2(BF_4)_4$; L = $ReCl(N_2)Ph_2P(CH_2)_2(PPh_2)_2$; M = $ReCl(N_2)(PMe_2Ph)_4$; N = $(PMe_2Ph)_4ClRe(N_2)CrCl_3(THF)_2$; O = $OsCl_2(N_2)(PEt_2Ph)_3$; P = $ReCl(CO)_2(N_2)(PPh_3)_2$; Q = $Ni_{cl}N_2$. References: A—G (this work); H (calculated shift); I (A. J. Rest, to be published); J (Yu. G. Borod'ko, A. K. Shilova, and A. E. Shilov, *Zhur. Fiz. Khim.*, 1970, **44**, 349; K—P (Prof. J. Chatt, personal communication); Q (R. P. Eischens and J. Jacknow, 'Proc. Int. Cong. on Catalysis,' Amsterdam, 1965, vol. I, p. 627)

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[19] R. van Hardeveld and A. van Montfoot, *Surf. Science*, 1966, **4**, 396.

[20] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[21] We have been unable to find in the literature a value for ν(NN) of $^{15}N_2$.

With due regard for these estimated errors we can see that the two carbonyl-containing dinitrogen complexes definitely lie off the straight-line plot and outside the limits of experimental error. The $^{14}N_2/^{15}N_2$ isotope shift is indicative of the amount of pure NN stretching in the normal mode corresponding to what would normally be described as ν(NN). Thus the shift for N_2 (admittedly a calculated shift assuming harmonic forces) lies above the line for the majority of the dinitrogen complexes. This is due to a small admixture in these systems of low-frequency modes of the same symmetry as ν(NN). In the case of $M_{cl}N_2$ and MN_2, assuming a linear MNN unit, there will be slight mixing of ν(MN) with ν(NN). However because of the errors in the observed shifts for these species and the theoretical value of the shift for elemental nitrogen it is not wise to calculate the bond–bond interaction constant $k_{MN,NN}$ from the deviations in the isotopic-shift data. For the carbonyl-containing dinitrogen complexes the shift from the line drawn through the other species is larger than their shift from the theoretical line through N_2(gas). This is clearly due to extensive mixing of the carbonyl stretching co-ordinate(s) with that of NN. Indeed in the compound $ReCl(CO)_2(N_2)(PPh_3)_2$ there is a sizeable dinitrogen isotope shift (*ca.* 25 cm^{-1}) in one of the predominantly 'CO-stretching' modes. A similar, but smaller effect is observed in one of the 'CO-stretching' modes of $Ni(CO)_3N_2$.

The observed frequencies and isotope shifts for the dinitrogen complexes described here are shown in Table 1.

TABLE 1

Nitrogen ($^{14}N-^{14}N$) stretching frequencies (cm^{-1}) for a number of binary metal dinitrogen complexes and their isotope shifts. [$\nu(^{14}N_2) - \nu(^{15}N_2) = \Delta$]

Metal	Cr	Ni	Pt	Cu
$M^{14}N_2$	2126·8	2169·4	2205·6	
Δ	70·7	73·0	74·0	
$M_{cl}{}^{14}N_2$	2089·8	2206	2230[b]	2272·2
Δ	69·8	74[a]		76·9
M_xN_2	2118·8	2188·3 2196·4		
Δ	70·7			

[a] R. P. Eischens and J. Jacknow, 'Proc. Int. Cong. on Catalysis,' Amsterdam, 1965, vol. 1, p. 627. [b] Ref. 19.

Using the CKFF [20] we have calculated values of the NN force constant for these species (Table 2). For comparison we show values for NiCO, $RuN_2(NH_3)_5I_2$, and N_2 itself. It is interesting to note that the NN bond appears to be of similar strength in both the molecular and cluster compounds of given M. The values of the NN force constants drop in the order Cu > Ni > Cr as is to be expected on a simple molecular orbital scheme from the values of the valence shell ionisation potentials of the metals.[22]

TABLE 2

Force constants (CKFF) of metal dinitrogen species (mdyn/Å)

Species	CrN_2	NiN_2	PtN_2	$Ni_{cl}N_2$	$Cu_{cl}N_2$
k_{NN}	18·65	19·41	20·06	20·07	21·29
Species	$Cr_{cl}N_2$	N_2	NiCO	$RuN_2(NH_3)_5I_2$	
k_{NN}	18·02	22·41	16·09[a]	16·48[b]	

[a] Ref. 6. [b] Yu. G. Borod'ko, A. K. Shilova, and A. E. Shilov, *Zhur. Fiz. Khim.*, 1970, **44**, 349.

Structure and Bonding.—We have only found one molecular dinitrogen complex for chromium, nickel, and platinum, and none for copper of formula MN_2. (The observations for copper however may be a result of the lack of *atomic* species in the matrix). Thus it seems that in contrast to carbon monoxide, dinitrogen prefers low co-ordination numbers in its binary compounds with metals. In experiments we have performed by co-condensing nickel atoms with carbon monoxide diluted with argon at 17 K (instead of the 4 K experiments of ref. 6) we see all four nickel carbonyls $Ni(CO)_{1-4}$. Using chromium atoms we see the hexacarbonyl and lower carbonyls.[4] Hence it is rather interesting to note that the maximum co-ordination numbers reached by the dinitrogen adducts, prepared in this way is the same for both chromium and nickel and less than their respective co-ordination numbers when carbon monoxide is used as the ligand.

Theoretical and experimental results for the metal-ligand bond in the carbonyls have shown it to be linearly bound through the carbon atom in an end-on arrangement M–C–O. Molecular orbital calculations [23] on FeN_2 prefer the linear arrangement Fe–N–N to the side-on alternative $Fe-\overset{N}{\underset{N}{|||}}$. All of the structural studies to date on metal dinitrogen complexes have indicated linear bonds.[24] We shall assume therefore that our N_2 complexes consist of a dinitrogen unit bound end-on as M–N–N. Parenthetically we note that the intensities of the NN stretches observed in this work seem quite high, as is to be expected for an end-on rather than a side-on geometry. In experiments using N_2 matrices containing some CO, the NN stretches were of comparable intensity to the carbonyl stretches of the $N(CO)_x$ species.[4]

There has been considerable argument concerning the relative π acceptor and σ donor properties of dinitrogen and carbon monoxide as ligands. Collman *et al.*[25] suggest, on the basis of relative changes in N_2 and CO stretching frequencies in analogous compounds, that dinitrogen is a more powerful π-acid than carbon monoxide. However, Bancroft *et al.*[26,27] from Mössbauer

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studies, suggest that CO is an appreciably better σ donor and/or π acceptor than N_2, and that N_2 is a better 'π–σ' ligand than CO.

Collman's result is not reflected in our work with CrN_2. The relative lowering of ligand stretching frequency in CrCO is larger than the same function for CrN_2 (see Table 3). For NiN_2 and NiCO the relative lowerings are equal. Moreover, as discussed above, fundamental donor/acceptor properties are more faithfully reflected in simple fragments than in the complexes considered by Collman. However, care must be exercised in interpreting this data. The ligand (CO or N_2) bond order will be dependent upon the nature of both the π^* and highest occupied σ orbitals of the ligand, and not just the former as considered by Collman *et al.* The highest occupied σ orbital in N_2 is approximately non-bonding (between NN) but its CO counterpart is CO antibonding in the free ligand.[28]

Table 3

Relative lowerings of ligand (NN or CO) force constants on metal complexation

Species	ν(CO) [a] cm^{-1}	L [b]	Species	(NN) [a] cm^{-1}	L [b]
NiCO	2000 [c]	0·13	NiN_2	2169 [d]	0·13
CrCO	1915 [e]	0·20	CrN_2	2126 [d]	0·17

[a] Frequencies observed in pure N_2 matrices. [b] $L = \dfrac{k_{CO}(\text{CO gas}) - k_{CO}(\text{CO complex})}{k_{CO}(\text{CO gas})}$, similarly for N_2. [c] J. K. Burdett (unpublished data). [d] This work. [e] Ref. 4.

It has recently been demonstrated that for carbon monoxide, the net effect of ligand complexation is to leave a positive charge on the metal. The results of an *ab initio* SCF–MO calculation [29] indicate a small positive charge (*ca.* 0·5) on the metal atom in $Ni(CO)_4$. *X*-Ray photoelectron data [30] also support an overall electron transfer from metal to ligand in metal carbonyls. Combined with the above observation that N_2 is a better 'π–σ' ligand than CO we should expect an even larger charge deficiency at the metal atom when dinitrogen is the ligand. This may be the prime factor in determining the low maximum co-ordination number observed by us for the binary metal dinitrogen complexes. The positive charge carried by the metal atom in $Ni(N_2)_x$ species when $x > 1$ may mean that these complexes are unstable and not formed even under matrix conditions. The only evidence we have for species where $x > 1$ is the weak perturbation of NiN_2 by N_2 in one of the matrix sites which could hardly be called a new chemical species. Complexes containing two dinitrogen units in addition to other ligands are however known; the N–N stretches of these bis adducts are rather low [often below 2000 cm^{-1}].[31]

In this light it is interesting to note the formation of metal–dinitrogen species, containing more than one metal atom, from photolysis of M/MN_2 mixtures in the nitrogen matrices reported in this work. This suggests that these species may be regarded as MN_2 to which another donor (M atom) has been attached, such that the charge deficiency on the metal bound to the dinitrogen is now shared by two metal atoms. This means that the bi (or tri) metal species are stable under the matrix conditions whereas the statistically more likely $M(N_2)_2$ or $M(N_2)_3$ species (nitrogen is present in considerable excess) are unstable and not observed. Similar arguments may be used to rationalise the ready formation of $M_{cl}N_2$. For CO where the metal ligand bonding seems to be considerably more synergistic such charge deficiency on the metal atom is not so pronounced and higher binary co-ordination numbers may be reached.

Conclusions.—The observation that co-condensation of metal atoms with pure nitrogen at 20 K leads to only one metal–dinitrogen complex is quite surprising, especially when under similar conditions carbon monoxide reacts to give several carbonyls. Collman's criterion for determining the magnitude of the π-acceptor properties of such ligands leads to the opposite result for CO and N_2 as ligands obtained previously by comparison of isostructural metal complexes of CO and N_2 stable at room temperature. Both π and σ bond effects seem therefore to determine the relative lowerings of the NN and CO stretching frequencies in such compounds.

It is suggested that lack of observation of metal–dinitrogen complexes beyond $M(N_2)$ is due to the large positive charge created on the metal atom when bound to the N_2 ligand.

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