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Binary Transition Metal Nitrogen Compounds; Infrared Evidence for $Ni(N_2)_x$

By J. K. BURDETT and J. J. TURNER*

(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary I.r. evidence suggests that nickel atoms react with nitrogen molecules in low temperature matrices to produce the dinitrogenyls of general formula $Ni(N_2)_x$ where x is probably 1 or 2.

IN recent years several compounds have been characterised containing a nitrogen molecule (dinitrogen) attached to a transition metal.[1] However, until now no species have been identified containing dinitrogen as the sole ligand.

Using the methods developed by Timms,[2] Andrews,[2a] Ogden,[3] and DeKock,[4] we have co-condensed nickel atoms with pure nitrogen and nitrogen–argon matrices in the temperature range 17—26 K using an Air Products AC 2L cryotip. The metal atom source consists essentially of a piece of pure metal nickel foil (Wiggin and Co.), electrically heated, situated *ca.* 10 cm from the low-temperature KBr window. The rate of deposition of the gas mixture through a separate inlet tube is controlled by a needle valve. Since the N–N stretching vibration of the nitrogen molecule is i.r. inactive, any i.r. bands appearing on spray-on are necessarily due to reaction of nickel atoms with nitrogen.

On spray-on with pure nitrogen ($^{14}N_2$, BOC Grade X; $^{15}N_2$ 96·3% enriched, Prochem Ltd.) at 20 K (indicated by a thermocouple imbedded in the central window with Wood's metal) two strong i.r. absorptions were observed: A at 2169·4 ($^{14}N_2$) and 2096·4 cm^{-1} ($^{15}N_2$), and B at 2179·8 ($^{14}N_2$) and 2106·2 cm^{-1} ($^{15}N_2$). The ratio of the optical densities A:B under these conditions was 2·1. Both these bands seem very stable to annealing and remained unchanged in intensity until the matrix boiled off at *ca.* 42 K. The variation in relative intensities of A and B in several experiments, with various deposition temperatures and dilutions of $^{14}N_2$ in argon, is summarised in the Table.

Thus the two i.r. bands A and B are due to two different nickel–dinitrogen species. If band A is assigned to $Ni(N_2)_x$ then B must be $Ni(N_2)_y$ (where $y > x$) since higher N_2:Ar ratios and higher deposition temperatures will favour the production of higher dinitrogenyls. Using a 1:1 mixture of $^{14}N_2$–$^{15}N_2$, in addition to the bands observed in pure $^{14}N_2$ and pure $^{15}N_2$ matrices, two bands 2177·2 and (2108·2 cm^{-1}) were observed. These latter two features were of the same intensity as the bands B. Thus a reasonable assignment for the quartet is: 2179·8 ($^{14}N_2Ni^{14}N_2$) 2177·2 ($^{14}N_2Ni^{15}N_2$) 2108·2 ($^{14}N_2Ni^{15}N_2$), and 2106·2 cm^{-1} ($^{15}N_2Ni^{15}N_2$). Further confirmation for this is that there was no evidence for extra bands that could be associated with bands A, *i.e.* A is due to $Ni(N_2)_1$.

Ratio of optical densities of band A *to band* B *under differing conditions of sample dilution and window temperature.*

	Deposition temperature (K)		
Matrix gas N_2:Ar	17	20	26
Pure nitrogen	2·5	2·1	1·2
1:4	—	10[a]	—
1:1500	—	?[b]	—

[a] B only appears as a shoulder on A. A is broader (*ca.* 6 cm^{-1} half-width) in a mixed matrix, than in pure nitrogen (*ca.* 2 cm^{-1}).
[b] No evidence for B.

The frequencies of A and B are closer to those for molecular nitrogen (2330 cm^{-1}) than is usually found for more stable dinitrogen complexes.[1] The $^{14}N_2$–$^{15}N_2$ shifts are: molecular nitrogen 81; $Ni(N_2)$, 73·0, and $Ni(N_2)_2$ 73·6 cm^{-1}. This implies a weak interaction between the nitrogen molecule and the nickel atom.

In several experiments, by raising the foil temperature, the rate of deposition of nickel atoms was greatly increased. With a dilute nitrogen–argon matrix, in addition to A and B a weak band appeared at 2206 cm^{-1}. Several workers[5–8] noted a strong band at 2202 cm^{-1} (ref. 5) due to sorbed nitrogen molecules (in the so-called γ_3 state[6]) on nickel atom clusters within a certain size range ($15 < d < 75$ Å).[7] In the high dilution experiments with high metal concentrations there is a much greater probability of nickel atoms linking to form clusters which can then pick up a dinitrogen than in the pure nitrogen matrix where $Ni(N_2)_x$

species are statistically more likely. It is interesting that Eischens and Jacknow[6] observed a $^{14}N_2$–$^{15}N_2$ shift for Ni_xN_2 of 74 cm^{-1}, almost identical to that reported above for $Ni(N_2)_x$.

With the increased foil temperature and pure $^{14}N_2$, an additional pair of bands appeared at 2188·3 (C) and 2196·4 cm^{-1} (*D*). These seem to be unrelated to any other spectral features. They disappear on annealing the sample to 26 K leaving the rest of the spectrum unchanged but may be regenerated by photolysis of the sample ($300<\lambda<330$ nm). [Since they are weak compared with bands A and B it is difficult to determine whether any increase in the amounts of $Ni(N_2)$ and $Ni(N_2)_2$ occurs on annealing.] As they only occur with heavy metal concentrations, they are probably dinitrogen complexes containing more than one nickel atom, *e.g.* $Ni_x(N_2)_y$ where x and y are both low numbers. It is interesting that the frequencies of the C and D features lie between those assigned to the mono-nickel species (A,B) and the band at 2206 cm^{-1} ascribed to Ni_xN_2.

We have also co-condensed chromium atoms with nitrogen and have evidence for $Cr(N_2)_x$ species.[9] Work is in progress condensing metal atoms with other ligands.

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