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Preliminary communication

IR evidence for tricarbonyl(dinitrogen) nickel, $Ni(CO)_3(N_2)$, in a nitrogen matrix at 20 K

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Structural studies[1] of dinitrogen complexes have shown that two types of bonding can occur, either terminal, *i.e.* M—N≡N, or linearly bridging two metals, *i.e.* M—N≡N—M′. Kinetic studies[2] have inferred the existence of a $M\leftarrow\overset{N}{\underset{N}{|||}}$ species as a transition state or short living intermediate. The matrix isolation technique[3] has provided spectroscopic evidence for a variety of unstable species and here I present IR evidence for the formation of $Ni(CO)_3(N_2)$, an example of a new kind of complex, in a nitrogen matrix.

Photolysis of a matrix mixture of $Ni(CO)_4$ and $^{14}N_2$ (1/5000) at 20 K with a medium pressure Hg arc and Cl_2 gas filter produced new IR bands at 2027, 2031, 2098, 2139 and 2266 cm^{-1}. The band at 2139 cm^{-1} corresponds to CO liberated during photolysis[4]. The other bands, which increased and decreased in intensity, which depended on the photolytic source used, with constant relative intensities, can be assigned to a single molecular species Ia. Photolysis of $Ni(CO)_4$ in a $^{15}N_2$ matrix under similar conditions gave new IR bands at 2027, 2031, 2096 and 2193 cm^{-1} (Ib) and a band due to CO.

The shift of the 2266 cm^{-1} band in a $^{14}N_2$ matrix to 2193 cm^{-1} for a $^{15}N_2$ matrix indicates that this band is a NN stretching band. The bands in the 2000–2100 cm^{-1} region are typical of terminal CO bands and the small separation between the bands at 2030 cm^{-1} suggests that they probably arise from a single vibrational mode. Similar splittings have been observed for a number of molecules, *e.g.* $Ni(CO)_4$ and $Co(CO)_3(NO)$ (Table 1) and may be accounted for by a matrix effect or a slight distortion of the molecule[5].

The NN and two terminal CO vibrations suggest three possibilities for I: (i) $Ni_x(CO)_y(N_2)_z$ with $x > 1$; (ii) $Ni(CO)_2(N_2)$; (iii) $Ni(CO)_{4-x}(N_2)_x$ with $x = 1$ or 2. The polynuclear complex (i) can be eliminated because the number and relative intensities of the bands did not change when the ratio of $Ni(CO)_4/N_2$ was varied from 1/2000 to

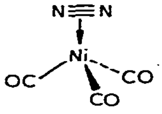
1/15000★. The coordinatively unsaturated species $Ni(CO)_2(N_2)$ (ii) and the bis-dinitrogen complex $Ni(CO)_2(N_2)_2$ (iii) are unlikely because of (a) the disparity in expected relative intensities of the CO vibrations, 3/1 and 2/1 respectively from isostructural model compounds $Co(CO)_2(NO)$ and $Fe(CO)_2(NO)_2$, with the observed value 8/1, and (b) other species should also have been observed with different photolysis sources[4a] or when the matrix was annealed[4b]. The IR data are consistent with $Ni(CO)_3(N_2)$ and show a strong similarity to $Co(CO)_3(NO)$ both in band relative intensities and in the splitting of the more intense CO vibration (Table 1).

TABLE 1

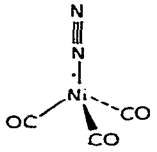
IR BAND POSITIONS (cm^{-1}) IN N_2 MATRICES AT 20 K

Compound		*ν(CO)*	*ν(NN)*
$Ni(CO)_4$	2047 2052 } T_2		
$Ni(CO)_3(^{14}N_2)$ (Ia)[a]	2027 2031 } E(16)	2098 A_1 (2)	2266 A_1 (1)
$Ni(CO)_3(^{15}N_2)$ (Ib)	2027 2031 } E	2096 A_1	2193 A_1
$Co(CO)_3(NO)$[a]	2036 2041 } E(7)	2106 A_1 (1)	

[a] Approximate relative intensities.



(A)



(B)

The structure A seems a possibility because of the high value of ν(NN) (only 65 cm^{-1} below free N_2) and the three terminal CO bands which would be consistent with the C_s symmetry of A. The relative intensity of the NN vibration (Table 1), however, is more consistent with a terminal NN vibration as for B than the extremely weak absorption expected for A[1], while the CO band pattern shows a strong similarity to $Co(CO)_3(NO)$ which is isostructural (C_{3v}) with B. It seems probable, therefore, that $Ni(CO)_3(N_2)$ has structure B.

Preliminary studies[6] of the photolysis of other transition metal carbonyls and their derivatives $M(CO)_aX_b$ ($X = H, CH_3, Br, NO, \pi\text{-}C_5H_5$) in N_2 matrices indicate that replacement of CO by N_2 is a general process and that the compounds represent a new type of dinitrogen complex.

★At the highest dilution aggregates of $Ni(CO)_4$ are unlikely to be formed on deposition of the sample and the high degree of isolation prevents aggregation during photolysis.

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