Determination of the Structure of Tetracarbonylnitrosylmanganese by Matrix Isolation Studies

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Summary Matrix isolation studies, including ^{13}CO enrichment, have demonstrated that the i.r. spectrum of [Mn(CO)$_4$NO] is consistent with C_{2v} symmetry (trigonal bipyramid with equatorial NO ligand) in accordance with *X*-ray crystallographic studies; the work resolves the disparity between previous solution i.r. studies (C_{3v}) and *X*-ray studies (C_{2v}).

IN spite of the widespread and successful use of i.r. spectroscopy as a tool for determining the structure of metal carbonyl and related compounds,[1] some important instances are known where the conclusions drawn from i.r. spectra are at variance with those from other techniques, *e.g.* [Fe$_3$(CO)$_{12}$] and [Mn(CO)$_4$NO]. According to *X*-ray crystallographic studies[2] [Mn(CO)$_4$NO] has a trigonal bipyramidal structure with an equatorial nitrosyl ligand and C_{2v} symmetry whereas, because three terminal CO-stretching bands were observed rather than the four expected for the C_{2v} geometry, a trigonal bipyramidal structure with an axial nitrosyl and C_{3v} symmetry was postulated[3] from the solution i.r. spectra.

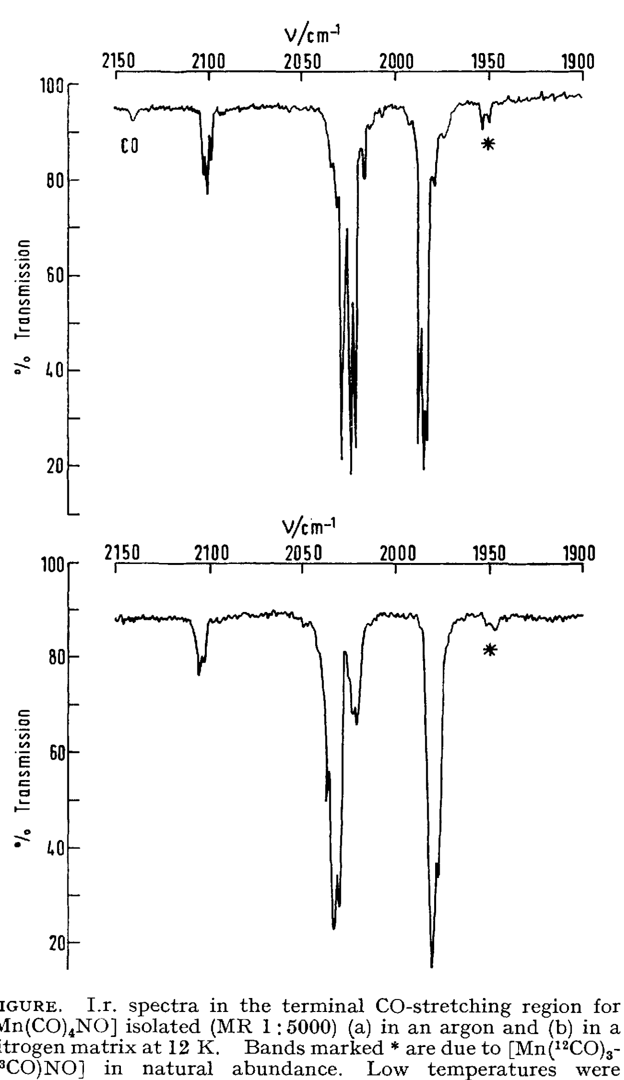

FIGURE. I.r. spectra in the terminal CO-stretching region for [Mn(CO)$_4$NO] isolated (MR 1:5000) (a) in an argon and (b) in a nitrogen matrix at 12 K. Bands marked * are due to [Mn(^{12}CO)$_3$(^{13}CO)NO] in natural abundance. Low temperatures were obtained using an Air Products Displex CSA-202 refrigerator.

The Figure shows spectra in the terminal CO-stretching region for [Mn(CO)$_4$NO] in argon and nitrogen matrices. The spectra are significant in two respects: (i) In an argon matrix three bands are observed for [Mn(^{12}CO)$_4$NO] in agreement with the solution studies, but the half-width at half-height of the band at *ca.* 2030 (10 cm^{-1}) cm^{-1} is considerably greater than the half-widths of the other two bands [5 cm^{-1} (2100 cm^{-1}); 5 cm^{-1} (1980 cm^{-1})]. This indicates that the absorption at *ca.* 2030 cm^{-1} may be due to two overlapping fundamentals. (ii) In a nitrogen matrix the band at *ca.* 2030 cm^{-1} is clearly resolved into two components. Matrix splittings[4] are typically in the range 0—8 cm^{-1} so that the two components (12 cm^{-1} separation between band centres) probably correspond to two fundamentals with the multiple splittings observed under higher resolution resulting from matrix effects.

Assigning the split band (2021·4, 2033·2 cm^{-1}) in an N$_2$ matrix as a single fundamental (*cf.* argon matrix and solution spectra) and taking a weighted wavenumbers position for it (2029·3 cm^{-1}), a reasonable set[1] of force constants were obtained in a Cotton–Kraihanzel force field ($k_e = 1682{\cdot}1$, $k_a = 1652{\cdot}3$, $k_{ae} = 55{\cdot}6$, and $k_{ee} = 19{\cdot}3$ N m^{-1}), which produced the observed frequencies for a C_{3v} [Mn(^{12}CO)$_4$NO] molecule (A_1, 2104·7; E, 2029·3; A_1, 1980·8 cm^{-1}). These force constants, however, when applied to the two mono-enriched forms of [Mn(^{13}CO)(^{12}CO)$_3$NO] (C_s, C_{3v}, NO axial) would not reproduce the observed frequencies (Table). The most noticeable differences were in equatorially enriched [Mn(^{13}CO)(^{12}CO)$_3$NO] where predicted bands at 1969·2 and 2002·5 cm^{-1} did not appear in the observed spectrum.

Assigning the terminal CO-stretching bands in N$_2$ matrices as the four (A_1, B_1, A_1, and B_2) i.r. active bands expected for C_{2v} symmetry, reasonable[1] values were obtained for the force constants (Table). Using these force constants, isotope spectra were calculated for the two C_s forms of mono-enriched [Mn(^{13}CO)(^{12}CO)$_3$NO] species (NO equatorial) and compared with the spectrum obtained for a ^{13}CO enriched sample[5] in an N$_2$ matrix. The excellent agreement (Table) between calculated and observed bands supports the conclusions drawn from *X*-ray crystallography that [Mn(CO)$_4$NO] has a trigonal bipyramidal structure with C_{2v} symmetry and an equatorial NO ligand.

The disparity between previous structural studies can be attributed to the failure[3] to resolve the four terminal CO-stretching fundamentals in the solution and gas-phase i.r. spectra. The results obtained for [Mn(CO)$_4$NO] in matrices

Table

Observed[a] and calculated[b] wavenumbers (cm^{-1}) for isotopically substituted [Mn(CO)$_4$NO] complexes (C_{2v} geometry)

Complex	Symmetry		Observed	Wavenumbers used in calculations	Calculated
[Mn(^{12}CO)$_4$NO]	C_{2v}	A_1	2105·3 2104·4 2102·1	2104·0	2103·3
		B_1	2037·3 2034·6 2033·3 2032·2 2030·4 2029·4	2033·2	2033·1
		A_1	2024·7 2023·0 2021·0	2021·4	2021·4
		B_2	1982·9 1980·0 1977·7	1980·0	1979·8
[Mn(^{12}CO)$_3$(^{13}CO)NO] (axial ^{13}CO)	C_s	A'	*ca.* 2091·2	2091·2[c]	2093·4
		A'	*ca.* 2025·3	2025·6[c]	2025·3
		A'	1997·3 1994·2 1990·7	1993·3	1993·5
		A''	1983·0 1980·4 1977·3	1980·2[d]	1979·8
[Mn(^{12}CO)$_3$(^{13}CO)NO] (equatorial ^{13}CO)	C_s	A'	2099·2 2096·7 2095·5	2097·4	2097·1
		A''	2036·1 2032·1 2030·0	2032·4[d]	2033·1
		A'	2012·6 2010·0	2011·3[c]	2012·4
		A'	1956·7 1951·4 1947·0	1950·1	1950·2

[a] N_2 matrix. [b] k_a = 1702·7, k_e = 1641·3, k_{aa} = 33·6, k_{ae} = 32·9, and k_{ee} = 58·6 N m^{-1}, where a = axial and e = equatorial. [c] Band partially obscured by overlap. [d] Band degenerate with [Mn(^{12}CO)$_4$NO] parent band in the CO-factored approximation.

at 12 K demonstrate the advantages and importance of matrix isolation as a technique for obtaining high quality i.r. spectra.

We thank the S.R.C. for a grant (to A.J.R. for the purchase of a modified Grubb Parsons Spectromajor I.R. Spectrometer) and for a studentship (to D.J.T.).

(*Received*, 25*th March* 1977; *Com.* 281.)

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