

Matrix Infrared Spectra of Manganese and Iron Isocyanide Complexes

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Complete citation for reference 16

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.01; Gaussian, Inc.: Wallingford, CT, 2009.

Calculated frequencies (cm⁻¹) and intensities (km/mol, in parenthesis) of M(CN)_x and M(NC)_x (M=Mn, Fe; x=1, 2).

MnCN

⁷Σ⁺

MnCN 151.5(2), 151.5(2), 383.5(95), 2225.4(50)

Mn¹³CN 147.2(2), 147.2(2), 378.9(93), 2176.9(44)

MnC¹⁵N 150.2(2), 150.2(2), 378.3(92), 2192.7(53)

MnNC

⁷Σ⁺

MnNC 108.1(1), 108.1(1), 444.5(123), 2101.0(396)

MnN¹³C 106.8(0), 106.8(0), 438.5(119), 2058.8(396)

Mn¹⁵NC 105.6(1), 105.6(1), 439.3(121), 2066.9(371)

Mn(CN)₂

⁶Σ_g⁺

Mn(CN)(CN) 57.1(30), 57.1(30), 198.9(0), 198.9(0), 235.4(12), 235.4(12),
372.2(0), 494.9(166), 2234.8(0), 2235.2(136)

Mn(¹²CN)(¹³CN) 57.1(30), 57.1(30), 195.8(0), 195.8(0), 232.2(11), 232.2(11),
368.9(0), 492.8(165), 2185.7(60), 2235.0(69)

Mn(¹³CN)(¹³CN) 57.0(30), 57.0(30), 193.2(0), 193.2(0), 228.4(11), 228.4(11),
365.7(0), 490.1(164), 2185.5(0), 2186.0(122)

Mn(C¹⁴N)(C¹⁵N) 56.5(29), 56.5(29), 198.1(0), 198.1(0), 234.9(12), 234.9(12),
368.5(0), 492.4(164), 2202.5(69), 2235.0(69)

Mn(C¹⁵N)(C¹⁵N) 55.9(29), 55.9(29), 197.2(0), 197.2(0), 234.3(12), 234.3(12),
364.9(0), 489.7(162), 2202.3(0), 2202.7(140)

Mn(NC)₂⁶Σ_g⁺

Mn(NC)(NC)	63.1(27), 63.1(27), 151.8(0), 151.8(0), 195.7(16), 195.7(16), 424.2(0), 569.6(224), 2092.4(911), 2104.8(0)
Mn(N ¹² C)(N ¹³ C)	62.3(26), 62.3(26), 150.9(0), 150.9(0), 195.2(16), 195.2(16), 419.9(0), 566.6(220), 2056.2(582), 2099.5(325)
Mn(N ¹³ C)(N ¹³ C)	61.5(26), 61.5(26), 150.0(0), 150.0(0), 194.8(17), 194.8(17), 415.7(0), 563.5(217), 2050.9(903), 2063.4(0)
Mn(¹⁴ NC)(¹⁵ NC)	63.1(27), 63.1(27), 150.0(0), 150.0(0), 193.4(15), 193.4(15), 420.4(0), 567.2(223), 2063.0(576), 2099.6(309)
Mn(¹⁴ NC)(¹⁵ NC)	63.1(27), 63.1(27), 148.3(0), 148.3(0), 190.8(15), 190.8(15), 416.8(0), 564.7(222), 2058.2(859), 2070.0(0)

FeCN⁶Δ

FeCN	160.8(3), 160.8(3), 401.2(92), 2225.7(75)
Fe ¹³ CN	156.2(3), 156.2(3), 396.4(90), 2176.9(66)
FeC ¹⁵ N	159.4(3), 159.4(3), 395.8(90), 2193.1(77)

FeNC⁶Δ

FeNC	116.5(1), 116.5(1), 465.2(117), 2094.5(453)
FeN ¹³ C	115.2(1), 115.2(1), 458.7(113), 2052.7(451)
Fe ¹⁵ NC	113.8(1), 113.8(1), 459.7(115), 2060.3(425)

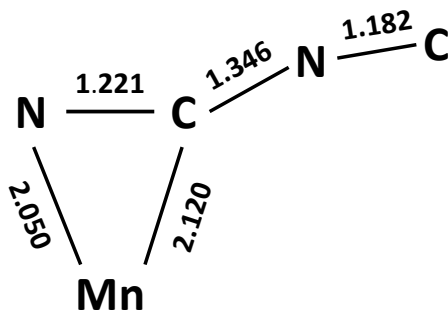
Fe(CN)₂⁵Δ_g

Fe(CN)(CN)	51.6(28), 51.6(28), 200.7(0), 200.7(0), 228.0(8), 228.0(8), 387.9(0), 513.2(184), 2231.8(222), 2231.9(0)
Fe(¹² CN)(¹³ CN)	51.6(28), 51.6(28), 197.4(0), 197.4(0), 225.0(8), 225.0(8), 384.4(0), 511.1(182), 2182.5(101), 2231.8(111)
Fe(¹³ CN)(¹³ CN)	51.5(28), 51.5(28), 194.9(0), 194.9(0), 221.3(7), 221.3(7), 381.0(0), 508.8(181), 2182.5(0), 2182.5(201)
Fe(C ¹⁴ N)(C ¹⁵ N)	51.1(27), 51.1(27), 199.9(0), 199.9(0), 227.4(8), 227.4(8), 384.0(0), 510.6(182), 2199.6(114), 2231.8(110)
Fe(C ¹⁵ N)(C ¹⁵ N)	50.6(27), 50.6(27), 199.0(0), 199.0(0), 226.7(9), 226.7(9), 380.2(0), 507.8(179), 2199.5(226), 2199.7(0)

Fe(NC)₂⁵Δ_g

Fe(NC)(NC)	63.8(23), 63.8(23), 153.7(0), 153.7(0), 198.9(14), 198.9(14), 442.0(0), 590.0(240), 2086.9(1095), 2103.7(0)
Fe(N ¹² C)(N ¹³ C)	62.9(22), 62.9(22), 152.8(0), 152.8(0), 198.5(15), 198.5(15), 437.5(0), 586.9(236), 2052.5(749), 2097.0(341)
Fe(N ¹³ C)(N ¹³ C)	62.1(22), 62.1(22), 151.9(0), 151.9(0), 198.0(15), 198.0(15), 433.1(0), 583.5(233), 2045.7(1085), 2062.6(0)
Fe(¹⁴ NC)(¹⁵ NC)	63.8(23), 63.8(23), 151.8(0), 151.8(0), 196.5(14), 196.5(14), 438.1(0), 587.5(239), 2058.8(746), 2097.2(319)
Fe(¹⁵ NC)(¹⁵ NC)	63.8(23), 63.8(23), 150.1(0), 150.1(0), 193.9(13), 193.9(13), 434.3(0), 584.9(238), 2052.6(1034), 2068.7(0)

Calculated geometries (bond lengths in angstrom units), energies (relative to $\text{Mn}(\text{CN})_2$), frequencies (cm^{-1}) and intensities (km/mol , in parenthesis) of $\text{Mn}(\text{CN})_2$ isomers at the B3LYP level of theory.



$$\angle \text{NCN} = 141.2^\circ$$

$$\angle \text{CNC} = 172.1^\circ$$

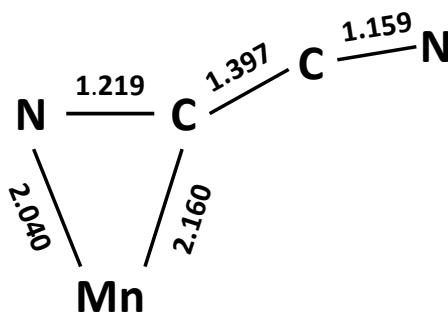
$$\angle \text{MnNC} = 76.2^\circ$$

$$\angle \text{MnCN} = 69.8^\circ$$

$$\angle \text{NMnC} = 34.0^\circ$$

$${}^6\text{A} \quad + 68.5 \text{ kcal/mol}$$

MnNCNC	411.5(2)	582.6(74)	927.1(64)	1857.9(22)	2126.6(299)
$\text{MnN}^{13}\text{CN}^{13}\text{C}$	401.3(2)	572.3(77)	903.5(58)	1813.1(21)	2089.2(292)
$\text{Mn}^{15}\text{NC}^{15}\text{NC}$	406.7(2)	571.8(67)	915.5(65)	1834.4(22)	2087.7(286)



$$\angle \text{NCC} = 144.7^\circ$$

$$\angle \text{CCN} = 174.1^\circ$$

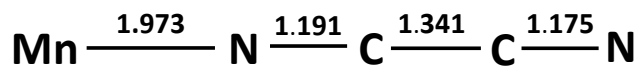
$$\angle \text{MnNC} = 78.6^\circ$$

$$\angle \text{MnCN} = 67.8^\circ$$

$$\angle \text{NMnC} = 33.6^\circ$$

$${}^6\text{A}' \quad + 46.6 \text{ kcal/mol}$$

MnNCNC	507.3(0)	567.2(18)	872.3(2)	1883.0(37)	2290.8(41)
$\text{MnN}^{13}\text{C}^{13}\text{CN}$	489.0(0)	550.4(19)	856.0(2)	1839.0(36)	2234.3(38)
$\text{Mn}^{15}\text{NCC}^{15}\text{N}$	505.9(0)	562.4(16)	856.4(2)	1857.6(35)	2263.0(40)



${}^6\Pi$ + 49.1 kcal/mol

MnNCCN	612.1(1)	969.9(6)	2040.3(19)	2220.1(717)
MnN ¹³ C ¹³ CN	590.6(0)	960.2(7)	1997.7(17)	2154.6(675)
Mn ¹⁵ NCC ¹⁵ N	609.9(1)	944.7(5)	2008.6(20)	2202.4(705)



${}^6\Sigma^+$ 0 kcal/mol (CCSD(T): + 1.8 kcal/mol)

NCMnNC	537.3(192)	2096.8(482)	2235.9(55)
N ¹³ CMnNC	536.1(190)	2096.8(483)	2186.2(48)
NCMnN ¹³ C	533.0(187)	2055.3(477)	2235.8(56)
N ¹³ CMnN ¹³ C	531.8(187)	2055.3(477)	2186.6(49)
¹⁵ NCMnNC	535.9(190)	2096.8(483)	2203.3(56)
NCMn ¹⁵ NC	533.7(191)	2062.4(453)	2235.8(56)
¹⁵ NCMn ¹⁵ NC	532.2(189)	2062.4(454)	2203.3(57)