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LOW FREQUENCY (200–700 CM^{-1}) SPECTRA OF MANGANESE CARBONYL DERIVATIVES OF THE TYPE Mn(CO)$_5$L

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INTRODUCTION

The vibrational spectra of metal carbonyls and their derivatives have been extensively studied particularly in the carbon–oxygen stretching region, and the frequencies of these vibrations have been correlated with the acceptor abilities of the ligands and with the degree of substitution of the carbonyl complex[1,2]. Following a recent study[3] of the metal–carbon stretching [ν(MC)] and metal–carbon–oxygen bending vibrations [δ(MCO)] in some metal carbonyl halides and their derivatives, we have extended this work to a series of complexes of manganese carbonyl of the type Mn(CO)$_5$L where L = H, CH$_3$, CD$_3$, C$_6$H$_5$, C$_6$H$_5$CH$_2$, Cl, Br or I, and to the parent manganese carbonyl. Accurate values for the band maxima in the 200–700 cm^{-1} region have been obtained for all these complexes, both in carbon tetrachloride and in cyclohexane. In addition comparable low frequency scans of the compounds [Mn(CO)$_6$]$^+$BF$_4^-$ and Et$_4$N$^+$[V(CO)$_6$]$^-$ have been obtained for Nujol mulls of these compounds. The number of ν(MC) and δ(MCO) modes active in the infrared is compared with the number expected on symmetry grounds, and their frequencies are correlated where possible with the frequencies of the ν(CO) modes.

RESULTS AND DISCUSSION

The results of the investigation are given in Table 1, in which the band maxima are reported in wavenumbers, followed in parentheses by the intensity of the band on an arbitrary scale in which the strongest band in the spectrum is equated to ten. For octahedral complexes of the type M(CO)$_6$, four fundamental vibrations are active in the infrared, each of symmetry t_{1u}. These modes can be described approximately as carbon–oxygen stretching modes (~ 2000 cm^{-1}), metal–carbon–oxygen bending modes (~ 600 cm^{-1}), metal–carbon stretching modes (~ 400 cm^{-1}), and carbon–metal–carbon bending modes (~ 100 cm^{-1})[4]. Accordingly, the strong bands at 416 and 460 cm^{-1} in the spectra of [Mn(CO)$_6$]$^+$ and [V(CO)$_6$]$^-$ are assigned as ν(MC) modes, while the strong bands at 637.5 and 646 cm^{-1} in the respective spectra are assigned as δ(MCO) modes. These data, together with the ν(CO) modes for the above compounds and for chromium hexacarbonyl, are summarised in Table 2.

While the δ(MCO) modes are not greatly affected by a change in the formal positive charge on the metal atom, there is clearly a reciprocal relationship between the frequencies of the ν(CO) and ν(MC) modes. This result is in complete agreement

TABLE 1

ABSORPTION BANDS IN THE 350–750 CM^{-1} REGION FOR SUBSTITUTED DERIVATIVES OF MANGANESE CARBO

$HMn(CO)_5$	a	362 (3)			462 (6)		
$CH_3Mn(CO)_5$	a				461.2 (4)		
	b				462.7 (4)		
$CD_3Mn(CO)_5$	a				458.3 (4.5)		
	b				457.5 (4)		
$PhMn(CO)_5$	a				454.4 (5)		
	b				455.0 (5)	466.8 (2.5)	502.5 (0
$PhCH_2Mn(CO)_5$	a				457.0 (4)		
	b				457.8 (4)	479.6 (sh)	
$Mn(CO)_5Cl$	a	399.7 (0.8)	412.0 (0.8)		466.9 (2.5)		
	b	400.6 (1.0)	412.0 (1.8)		469.4 (2.4)		
$Mn(CO)_5Br$	a	398.1 (0.8)	410.9 (0.7)	420.9 (2.0)	466.2 (1.5)		
	b	399.4 (0.4)	411.2 (1.5)	420.9 (3.2)	467.5 (1.1)		
$Mn(CO)_5I$	a	399.0 (0.2)	411.2 (0.7)	431.6 (2.8)	467.8 (0.7)		
	b	400.0 (0.2)	411.3 (0.7)	433.1 (2.2)	469.1 (0.7)		
$Mn_2(CO)_{10}$	a	399.7 (1.3)		426.8 (0.3)	469.2 (4.1)		
	b	400.3 (2.0)		428.0 (0.3)	469.1 (5)		
$[Mn(CO)_6]^+BF_4^-$	c		416.2 (7)				500.8 (2
$Et_4N^+[V(CO)_6]^-$	c	398.7 (1.2)		421.3 (1.2)	460.0 (3.8)		
PhCl	a					466.2 (6)	
$PhCH_2Cl$	a					465.0 (1)	

[a] a = cyclohexane solutions; b = carbon tetrachloride solutions; c = Nujol mulls. Absorption maxima are given cm^{-1}, followed in parentheses by the peak intensity on a scale in which the strongest band is given the value ten. [b] $\nu_4(t_2)$ of the BF_4^- ion.

with current theories of π-bonding in metal carbonyls[1]. However, in the spectra of the compounds $[Mn(CO)_6]^+BF_4^-$ and $Et_4N^+[V(CO)_6]^-$ there are additional bands near 500 cm^{-1} in the first case, and near 400 cm^{-1} in the second case, which must arise from site-symmetry activation of ν(MC) and δ(MCO) modes inactive in strict O_h symmetry.

The vibrational spectra of the compounds of the type $Mn(CO)_5L$ present a much more difficult interpretative problem. As indicated previously[3], the distribution of normal modes of the type ν(MC) is $2a_1 + b_1 + e$, and of the type δ(MCO) is $a_1 + a_2 + b_1 + b_2 + 3e$ (the a_1 and e modes being infrared-active, assuming a molecular symmetry of C_{4v}). Thus seven bands in the spectra of all such derivatives are expected to be infrared-active in the 350–750 cm^{-1} region. It was hoped that it would prove possible to identify all the ν(MC) modes on the assumption of (*a*) a constant amount of π-bonding in the metal–carbon–oxygen system, *i.e.* of a reciprocal relationship between the ν(MC) and ν(CO) modes as discussed above and (*b*) on the assumption that the

TABLE 2

INFRARED ABSORPTION BANDS OF OCTAHEDRAL METAL CARBONYLS OF THE TYPE $M(CO)_6$ (cm^{-1})

	ν(*MC*)	δ(*MCO*)	ν(*CO*)
$Mn(CO)_6^+$	416	638	2101
$Cr(CO)_6$[b]	441	668	1981[a]
$V(CO)_6^-$	460	646	1859[a]

[a] Data from Ref. 1. [b] The values quoted are for the gaseous state; the corresponding values for $Cr(CO)_6$ in the solid state are 448 and 656 cm^{-1} respectively. The values for the ν(MC) and δ(MCO) modes of all three derivatives in CH_3CN solution lie within ± 3 cm^{-1} of these quoted.

		609 (9.5)	657 (10)	670 (5)		
			651.9 (9.5)	661.3 (9.6)		
(0.6)			650.6 (10)	660.3 (9)		
	587.9 (1.0)			663.4 (10)		
	586.9 (0.8)	627.5 (0.8)		660.9 (10)		
		629.4 (2)	656.9 (10)		700.6 (3)	
		630.0 (3)	656.8 (10)			
	555.3 (0.7)		646.8 (9)	655.6 (10)	696.7 (4)	
(2.6)	553.8 (0.8)	629.4 (sh)	646.2 (9)	654.1 (10)	698.9 (4)	
		602.3 (0.6)	643.3 (10)	647.5 (9)		
	547.2 (0.7)	603.1 (0.6)	642.3 (10)	648.0 (9)		
	546.2 (0.3)	600.0 (0.3)	642.2 (10)	646.8 (9)		
	546.9 (0.6)	603.7 (0.3)	642.0 (10)	646.8 (9)		
	546.3 (0.2)		641.3 (10)			
	548.1 (0.3)		641.6 (10)			
	556.9 (0.6)		642.2 (10)	647.9 (9)		
	556.9 (0.9)		642.5 (10)	648.1 (9.5)		
(4)^b			637.5 (10)			735.9 (2.3)
			646.3 (10)			
					683.1 (10)	703.7 (8)
	560.3 (2)					698.7 (10)

characteristic intensity pattern of the ν(CO) modes would be reproduced by the ν(MC) modes. However, it appears that these assumptions are not sufficient to explain all the features of the spectra.

The infrared-active ν(CO) modes of the relevant compounds in cyclohexane solutions are listed in Table 3, in order of decreasing value for the very strong mode of e symmetry. This mode only spans a 44 cm^{-1} range, while the a_1 modes span even smaller ranges (33 and 19 cm^{-1}). It appears a reasonable procedure to identify the band of medium strength in the 454–468 cm^{-1} range (*i.e.* the strongest band in the 200–600 cm^{-1} range) as the ν(MC) mode of e symmetry. Moreover, the band occurs with similar frequencies and intensities as the corresponding vibration of the parent $Mn_2(CO)_{10}$, which has been identified in a similar manner. However, it must be emphasised that in these molecules there is *no* regular relationship between the ν(MC) and ν(CO) modes thus identified. This is undoubtedly because the ligand (L) is only very slightly affecting the π-electron distribution in the metal–carbon–oxygen bond systems [as evidenced by the very slight frequency shifts of ν(CO) and especially of ν(MC) in each case] and presumably other factors (*e.g.* the mass of the ligand) are obscuring the expected simple relationship.

More surprising, however, is the appearance of varying numbers of bands below 460 cm^{-1}, when only one band would be expected in this region, namely, the a_1 ν(MC) mode corresponding to the symmetric vibrations of the four-in-plane CO groups (*cf.* Table 3). As all the compounds were analytically pure, and showed no extraneous peaks in the ν(CO) region, the possibility that the weak bands near 400 cm^{-1} in the spectra of the chloride, bromide, and iodide are due to impurities can be ruled out. Moreover, these bands appear both in cyclohexane and in carbon tetrachloride solutions

TABLE 3

CO STRETCHING FREQUENCIES IN DERIVATIVES OF THE TYPE $Mn(CO)_5L$

Solutions in cyclohexane; frequencies in cm^{-1}.

a_1^a is the symmetric vibration of the four in-plane CO groups; a_1^b is the vibration of the unique CO group.

	a_1^a	e	a_1^b	*Ref.*
$ClMn(CO)_5$	2138 w	2054 s	1999 m	14
$BrMn(CO)_5$	2133 w	2050 s	2001 m	14
$IMn(CO)_5$	2125 w	2044 s	2003 m	14
$C_6H_5Mn(CO)_5$	2114 w	2021 s	1997 m	15
$HMn(CO)_5$	2118 vw	2016 vs	2007 s	16
$C_6H_5CH_2Mn(CO)_5$	2106 w	2012 s	1992 m	this work
$CH_3Mn(CO)_5$	2109 w	2010 s	1989 m	15
$CD_3Mn(CO)_5$	2105 w	2010 s	1988 m	this work

at closely similar frequencies, but they have no counterparts in the spectra of the CH_3, CD_3, C_6H_5 and $C_6H_5CH_2$ derivatives. Solvent molecules might create a field of local symmetry lower than C_{4v} and in this way activate more $\nu(MC)$ modes. However, if such were the case, the $\nu(CO)$ modes should be affected in just the same way, *i.e.* more $\nu(CO)$ modes should be activated, and this is not observed. Moreover, it is not clear why such an effect should be specific to the halides but not to the alkyl and aryl derivatives. It is perhaps pertinent that while all molecules of the type $M(CO)_5L$ where L is a monodentate ligand are expected to have C_{4v} symmetry (those in which L is a polydentate ligand strictly have lower symmetries), there is no symmetry restriction on the axial-to-equatorial CMC bond angles (θ). Indeed in the hydride[5] these angles average 96.7°. With bulkier ligands they would be expected to decrease and may well be less than 90° for some of the halides. The degree of mixing of the axial and the equatorial $\nu(MC)$ modes is dependent on θ and thus the relative intensities of the modes would be expected to vary. A final decision on the origin of the weak bands near 400 cm^{-1} in the spectra of the halides must await a study below 200 cm^{-1} in order to check the possibility that they might arise from combination bands of low-lying fundamentals. The spectrum of the hydride appears to be normal in that it has a single band below 460 cm^{-1} (the a_1 vibration of the four in-plane carbonyl groups) albeit at the remarkably low frequency of 362 cm^{-1} (both in cyclohexane solutions and in the gaseous state[5]).

Several bands near 600 cm^{-1} in all the spectra are assigned as $\delta(MCO)$ modes, though as expected no correlation between the frequencies of these vibrations and the nature of the ligand is evident. One of the bands, near to 650 cm^{-1} in each case, is the strongest band in the low frequency spectrum, and must correlate with the $\delta(MCO)$ mode of the t_{1u} symmetry in metal hexacarbonyls. The interpretation of the other bands in this region is made more difficult because certain of the ligands (notably C_6H_5 and $C_6H_5CH_2$) themselves absorb in the 450–750 cm^{-1} region, as indicated in Table 1.

Corresponding bands in the spectra of the compounds at 470 cm^{-1} (and lower) typically lie 0–2.5 cm^{-1} higher for carbon tetrachloride than for cyclohexane solutions; although there is less regularity, the reverse is frequently true of the bands near 650 cm^{-1}. Further comment on these spectra is not justified at this stage.

EXPERIMENTAL

Synthesis of compounds

The derivatives were prepared according to methods described in the literature.

(*a*) $HMn(CO)_5$[7]. The product was purified by trap-to-trap distillation, and the spectrum below 400 cm^{-1} recorded by condensing the product into a polythene tube which could be sealed from the atmosphere.

(*b*) $CH_3Mn(CO)_5$[8]. The product was sublimed twice at 50° and atmospheric pressure to produce white needles, m.p. 95°, lit. value 94.5–95°.

(*c*) $CD_3Mn(CO)_5$. This compound was prepared as above, m.p. 95°. Bands occurring at 2999 (sh), 2968, 2916, and 2817 cm^{-1} in the spectrum of the methyl derivative were absent from the spectrum of the deutero species, but were replaced by bands at 2577 (w), 2500 (w), 2416 (w) and 2237 (s) cm^{-1}.

(*d*) $C_6H_5Mn(CO)_5$. This compound was prepared by decarbonylation of the benzoyl derivative. The latter was prepared by the method of Closson *et al.*[8] except that the sodium salt of manganese carbonyl was reacted with benzoyl chloride. The resultant solution was poured into iced water to yield a yellow crystalline product which was decarbonylated at 60° for 2 h. Sublimation at 50° *in vacuo* gave a yellow solid. This product was sublimed twice at 100° at atmospheric pressure to yield a white crystalline solid, m.p. 52°; lit. value 52°.

(*e*) $C_6H_5CH_2Mn(CO)_5$. This compound was prepared by the method of Closson *et al.*[8] using benzyl chloride in the reaction with the sodium salt of manganese carbonyl. On pouring the tetrahydrofuran solution of the product into iced water an oil was obtained. This was extracted with ether, the solvent evaporated, and the product sublimed twice in vacuo at 100° to yield a yellow crystalline product, m.p. 40°.

(*f*) $Mn(CO)_5Cl$[9], $Mn(CO)_5Br$[9] *and* $Mn(CO)_5I$[10]. These derivatives were resublimed in vacuo at 50° immediately before use.

(*g*) $[Mn(CO)_6]^+BF_4^-$ (*ref. 11*) *and* $Et_4N^+[V(CO)_6]^-$ (*ref. 12*). The latter compound was purified by dissolving in diglyme followed by precipitation by addition of petroleum ether (40–60°).

Infrared spectra

The infrared spectra of the compounds were recorded in cyclohexane and carbon tetrachloride solutions using a variable path length solution cell fitted with potassium bromide windows. A second variable path length cell was used for solvent compensation in the reference beam. The measurements were made using a Unicam SP 100 prism/grating spectrometer in the 375–750 cm^{-1} region, and using a Grubb–Parsons DM 2 spectrometer in the 200–455 cm^{-1} range. The Unicam instrument was calibrated by reference to the spectrum of indene and the peak positions should be accurate to ± 0.5 cm^{-1} "for sharp peaks". The spectra were recorded on the 12.5 cm^{-1}/cm scale at a scanning speed of 14 cm^{-1}/min. The Grubb–Parsons instrument was calibrated by reference to part of the rotational spectrum of water vapour. Spectra in the 2000 cm^{-1} region were recorded with a Grubb–Parsons GS 2A spectrometer, calibrated by reference to the carbon–nitrogen stretching mode[13] of acetonitrile (2253.5 cm^{-1}). The spectra of all the compounds were recorded in this region, and the carbon–oxygen stretching frequencies agreed with the published values.

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SUMMARY

The infrared spectra of derivatives of manganese carbonyl of the type $Mn(CO)_5L$ ($L = H, CH_3, CD_3, C_6H_5, C_6H_5CH_2, Cl, Br, I$) as well as of the parent carbonyl have been recorded in the 200–700 cm^{-1} region in cyclohexane and carbon tetrachloride solutions. In addition, the corresponding spectra of the ionic derivatives $[Mn(CO)_6]^+BF_4^-$ and $Et_4N^+[V(CO)_6]^-$ have been recorded as Nujol mulls. Assignments for the metal–carbon stretching and metal–carbon–oxygen bending modes are discussed with special mention of possible correlations with the relevant carbon–oxygen stretching modes.

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