Vibrational Spectra of Tricarbonyl(π-cyclopentadienyl)manganese, Bis[tricarbonyl(π-cyclopentadienyl)molybdenum], and their Deuteriated Derivatives

By **David J. Parker,** Chemistry Section, Norwood Technical College, London S.E. 27

The i.r. and laser Raman spectra of $(\pi\text{-}C_5H_5)Mn(CO)_3$, $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, and their deuteriated derivatives have been measured and assignments made. The data on the manganese complex reveal that interpretation of the solution spectrum of the C_5H_5-Mn moiety on the basis of C_{5v} ' local ' symmetry may only be regarded as an approximation. Product rule calculations have been carried out for the a_1 ring modes of both complexes. For the manganese complex only calculations have also been done for e_2 modes and have been used as an aid to assignment of the spectrum of the deuteriated derivative. The spectrum of $(\pi\text{-}C_5H_5)Mn(CO)_3$ has been studied as a gas (i.r. only), liquid, and solid (at room temperature and 77 K) and spectral differences arising from change of state and temperature discussed. The ' local ' symmetry approach has been shown to be no longer applicable for assignment of the spectrum of both complexes in the solid state. Methods used for obtaining the spectra are described.

PREVIOUSLY,[1,2] we reported the i.r. spectra of some π-cyclopentadienylmetal carbonyl complexes, measured as mulls and in solution, in the ranges 4000—550 [1] and 700—200 cm^{-1}.[2] Probable assignments of the vibrations of the cyclopentadienyl ring were made using our i.r. data together with incomplete Raman data on the manganese complex reported by Lippincott *et al.*[3] Certain assignments were still in doubt (*e.g.* for the e_2 CC stretching mode). To attempt to resolve doubtful assignments and to confirm previous work the complete Raman spectrum of $(\pi\text{-}C_5H_5)Mn(CO)_3$ has been measured. As an aid to assignment the Raman spectrum of its perdeuteriated derivative and of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and its perdeuteriated derivative have also been measured. Because of difficulties due to decomposition, the solution spectrum of $(\pi\text{-}C_5D_5)Mn(CO)_3$ has only been recorded at low concentrations. For the same reason, the Raman spectra of the molybdenum complex and its deuteriated derivative have only been measured in the solid state, with a detuned laser scource; consequently low intensity and high wavenumber bands have not been observed. The i.r. data on these complexes have been extended to include the spectrum of $(\pi\text{-}C_5H_5)Mn(CO)_3$ as a gas, liquid (at 353 K), and solid film (at 77 K). The spectra of the complexes, except $(\pi\text{-}C_5D_5)Mn(CO)_3$ have been recorded as CsI discs.

The vibrational spectrum of $(\pi\text{-}C_5H_5)Mn(CO)_3$ is given in Table 1 and that of its deuteriated derivative in Table 2. The vibrational spectra of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and its deuteriated derivative are given in Tables 3 and 4 respectively. The numbering system for assignment of π-cyclopentadienyl ring modes is that given previously.[1]

DISCUSSION

Band Assignment for (π-Cyclopentadienyl)tricarbonylmanganese and its Deuteriated Derivative.—(i) *π-Cyclopentadienyl ring vibrations.* Adams and Squire [4] have observed eight, rather than the predicted three, polarised Raman bands in the solution spectrum of $(\pi\text{-}C_5H_5)Mn(CO)_3$ and, together with the evidence that the i.r. spectrum shows more i.r. bands than predicted by C_{5v} ' local ' symmetry have concluded that this symmetry is not an adequate approximation. However, only five polarised Raman bands associated with ring modes have been observed in this work, bands assigned with ν_6 and ν_{11} being shown to be definitely depolarised. It is, therefore, suggested that, since only two of the ten predicted depolarised bands (*i.e.* those assigned to ν_{10} and ν_{14}) are polarised, the symmetry fairly closely approaches C_{5v} and that the ' local ' symmetry approach is still a reasonable approximation. It is, however, accepted that the solution spectrum of $(\pi\text{-}C_5H_5)Mn(CO)_3$ is not as simple as that of either ferrocene or ruthenocene and clearly C_{5v} local symmetry may only be regarded as an approximation.

Assignments are as given in the Tables and compare well with previous assignments for ferrocene,[5,6] [$^2H_{10}$]-ferrocene,[7] and ruthenocene.[8] Adams and Squire [4] have recently published an assignment for the spectrum of $(\pi\text{-}C_5H_5)Mn(CO)_3$ with no deuteriation data. Their assignments, with a few minor differences, are in agreement with those made here. Main differences from previous assignments and points arising from deuteriation studies are now discussed.

a_1 *Class.* Fundamentals of this class are readily identified by their polarisation characteristics in the Raman spectrum. Previously [1,3] it has not been possible satisfactorily to distinguish modes ν_2 and ν_7 which both occur *ca.* 850 cm^{-1}. Polarisation measurements clearly indicate that the lower frequency band at 837 cm^{-1} must be assigned to ν_2. The Redlich–Teller product rule [9] has been used to confirm assignments. The observed product ratio of 0·503 is in good agreement with the theoretical 0·510.

a_2 *Class.* Assignment of a band at 1266 cm^{-1} to the

---

[1] D. J. Parker and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1970, 480.

[2] D. J. Parker, *J. Chem. Soc.* (*A*), 1970, 1382.

[3] I. J. Hyams, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta*, 1967, **23A**, 273.

[4] D. M. Adams and A. Squire, *J. Organometallic Chem.*, in the press.

[5] T. V. Long and F. R. Huege, *Chem. Comm.*, 1968, 1239.

[6] D. Hartley and M. J. Ware, *J. Chem. Soc.* (*A*), 1969, 138.

[7] R. T. Bailey, *Spectrochim. Acta*, 1971, **27A**, 199.

[8] D. M. Adams and W. S. Fernando, *J.C.S. Dalton*, 1972, 2507.

[9] O. Redlich, *Z. phys. Chem.*, 1935, **28**, 371; E. Teller quoted by W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. T. Raisin, J. W. Thompson, and C. L. Wilson, *J. Chem. Soc.*, 1936, 971.

TABLE 1

Vibrational spectrum (cm^{-1}) of (π-C_5H_5)Mn(CO)$_3$

I.r. of CsI disc	I.r. solid film (77 K) †	Raman solid at room temperature	Intensity	Raman sublimed solid at 77 K	Intensity	I.r. liquid at 353 K †	I.r. of solution	Raman of liquid	ρ	Raman of solution	ρ	I.r. of gas ‡	Assignment
3132m,sh?	3134m	* 3132	100 ^{a}	* 3134	100 ^{a}	3132w				* 3125m	*ca.* 0		a_1 CH stretch (ν_1)
3124m		* 3121r.sh	24 ^{a}	* 3120	32 ^{a}	3127w	3122m ^{c}			* 3120w	depol.?	3105w	e_1 CH stretch (ν_5)
3104w,sh		* 3109r.sh	30 ^{a}	* 3105	33 ^{a}	3122w							e_2 CH stretch (ν_9)
		* 3098r.sh	24 ^{a}	* 3095	26 ^{a}								
n.m.	n.m.					n.m.	2685vvw ^{d}						(2027 + 666)
n.m.	n.m.					n.m.	2655vvw ^{d}						(2027 + 635)
n.m.	n.m.					n.m.	2600vvw ^{d}						(1944 + 666)
n.m.	n.m.					n.m.	2565vvw ^{d}						(2027 + 541)
n.m.	n.m.					n.m.	2510vvw ^{d}						(2027 + 494)
n.m.	n.m.					n.m.	2475vvw ^{d}						(1944 + 541)
n.m.	n.m.					n.m.	2430vw ^{d}						(1944 + 494)
2017vs,sh	2017vs												
2013vs		* 2014	85 ^{a}	* 2014	80 ^{a}	2022vvs	2027vs ^{e}	2020m	*ca.* 0	2027m	*ca.* 0	2041vs	a_1 CO stretch
1950vs,sh	1948vs					1956vs,sh?							
		* 1943	250 ^{a}	* 1943	170 ^{a}								
1935vs						1926vvs,br	1944vs ^{e}	1929m-s	0·74	1944m-s	0·72	1965vs	e CO stretch
1918vs	1916vs	* 1920	360 ^{a}	* 1919	180 ^{a}								
1910vs	1909vs	* 1914r.sh	80 ^{a}	* 1913r.sh	60 ^{a}								
	1889s?												
	1884s?												
1426s,sh }	1428m-s }	1426	26 } 36 ^{b}	1428	45 } 55 ^{b}	1423m-s	1425s ^{c}			1425w	0·72	1418m	e_1 CC stretch (ν_8)
1421s	1421m	1421r.sh	10	1421r.sh	10								
1360m	1360w	1360	13 ^{b}	1361	24 ^{b}					1364w	0·72		e_2 CC stretch (ν_{12})
1265w	1255w-m			1266	4 ^{b}	1258vw	1267w ^{c}					1256vw	a_2 CH bend ∥ (ν_4)
		1218	8 ^{b}	1220	10 ^{b}					1215vw	*ca.* 0		e_2 CH bend ∥ (ν_{10})?
1205w							1200w ^{c}						(541 + 666)
1152vw	1159w						1152w ^{c}					1140vw?	(494 + 666)
1114w-m,sp	1113w-m,sp	1114	280 ^{b}	1116	320 ^{b}	1114m,sp	1114m,sp ^{c}	1116vs	*ca.* 0	1117vs	*ca.* 0	1110vw	a_1 ring breathing (ν_3)
1064m-s }	1063m-s }	1065	45 } 85 ^{b}	1067	60 } 130 ^{b}	1064w	1062w,sh } ^{c}	1064w-m	0·70	1065w-m	0·80	1038vw,sh	e_2 CH bend ⊥ (ν_{11})
1058m-s	1058m-s	1059	40	1059	70		1051w-m						
1028vw							1029vw,sh ^{c}						(494 + 541)
1012m-s }	1014m-s }	1012r.sh	2 } 18 ^{b}	1013r.sh	4 } 30 ^{b}	1010m	1007s ^{c}			1010vw	0·71	1003m	e_1 CH bend ∥ (ν_6)
1007m-s,sh	1006w-m	1005	16	1006	26								
959vw													(2 × 488)
938m-s	944m-s	938 }	11 ^{b}	942	5·5 } 11 ^{b}		922w ^{c}						e_2 ring distortion ∥ (ν_{13})
		931sh		933	5·5								
910w-m,sh							906w ^{c}						(370 + 541)
860sh	865w?	858sh	4 } 27 ^{b}	863r.sh	7 } 38 ^{b}								
	853s }												
848vs	847s	844	23	848	31	840m,sh?	842m,sh ^{d}						e_1 CH bend ⊥ (ν_7)
837vs	836s	833	22 ^{b}	836	27 ^{b}	832s	831vs ^{d}			837w	*ca.* 0	830s	a_1 CH bend ⊥ (ν_2)
	834s												
667vs	670vs	663	21 ^{b}	670	22 ^{b}	664s-vs	666vs ^{e}			667w	*ca.* 0	661s	a_1 Mn–C–O bend
	655m												
639vs,sh	642s												
632vs	634vs	639	6 ^{b}	642	5 ^{b}	632vs	635vs ^{e}					631s	e Mn–C–O bend
609m-s	611m-s	608	16 ^{b}	610	24 ^{b}					616vw	*ca.* 0		e_2 ring distortion ⊥ (ν_{14})
	547vs,sh }												
543vs	544vs	544	35 } 42 ^{b}	546	45 } 53 ^{b}	537s-vs	541vs ^{e}			542w	0·75	533s	e Mn–C–O bend
		537r.sh	7	541r.sh	8								
500m	505m }	503	240 ^{b}	502	315 ^{b}			494s	0·15	493s	*ca.* 0	495w	a_1 Mn–CO stretch
	502m,sh												
488m	491m }	487r.sh	110 ^{b}	489	135 ^{b}		494w ^{e}						
	488m,sh							488m	*ca.* 0·70	491m	depol?	488w	e Mn–CO stretch
386vs,sh }		387	65 } 155 ^{b}	390	95 } 210 ^{b}								
372w-m		369	90	370	115		370w ^{c}	372w,sh	depol?				e_1 ring tilt
356vw,sh		355	1000 ^{b}	356	1000 ^{b}		355vw,sh? ^{c}	347vs	*ca.* 0	348vs	*ca.* 0		a_1 ring-Mn stretch
		135r.sh	85 } 3050 ^{b}	137r.sh	116 } 3060 ^{b}								
		128r.sh	190										
		118	1765	121r.sh	1375			111vs,sh }	0·76	111vs,sh }	0·71		OC–Mn–CO bends +
		112sh	240	114	850			101vs		104vs			ring-Mn–CO bends
		100r.sh	590	100r.sh	560								
		89r.sh	120	90r.sh	60								
				85sh?	40								
		77r.sh	60										
				75	180 ^{b}								
				59	220 ^{b}								
				56	90 ^{b}								
		46	95 ^{b}										

* Measured using the 568·2 nm line, remaining bands measured using the 647·1 nm line. † Using AgCl plates. ‡ Using KBr plates. n.m. = Not measured. ρ Degree of depolarization.

^{a} Intensity of 3130 cm^{-1} band at 100 units (corrected for changes in response). ^{b} Intensity of 355 cm^{-1} band at 1000 units (corrected for changes in response). ^{c} Dissolved in CCl_4 (except bands at *ca.* 3100 and below 400 cm^{-1} from ref. 1). ^{d} Dissolved in CS_2 (from refs. 1 and 2). ^{e} Dissolved in n-hexadecane from refs. 1 and 2).

TABLE 2

The vibrational spectrum (cm^{-1}) of (π-C_5D_5)Mn(CO)$_3$

I.r. of Nujol mull	Raman of solid at room temperature	Raman of sublimed solid at 77 K	Intensity	I.r. of solution	Raman of CCl_4 solution	Assignment
* 3120vvw [a]				* 3110vvw [b]		(2023 + 629)
n.m.				2655vvw [c]		(2023 + 540)
n.m.				2565vvw [c]		(2023 + 488)
n.m.				2510vvw [c]		(1940 + 540)
n.m.				2475vw [c]		(1940 + 488)
n.m.				2430vw [c]		
	2355w	2355	210		2349w (0·24)	a_1 CD stretch (ν_1)
2345m [a]	2349w,sh			2340m [b]		e_1 and e_2 CD stretches (ν_5 and ν_9)
n.m.	n.m.	2016	180	n.m.	2023m (*ca.* 0)	a_1 CO stretch
n.m.	n.m.	1944	330			
n.m.	n.m.	1921	420	n.m.	1940m (0·74)	e CO stretch
n.m.	n.m.	1915r,sh	190			
1330vw [a]	1337vw	1336	35			
1313m [a]	1313vw,sh	1316	15	1311m [b]		e_1 CC stretch (ν_8)
1306m,sh [a]	1304vw	1305	17			
1270w,sh						
		1256	19	1260m? [b]		e_2 CC stretch (ν_{12})
		1239	14			
1230vw [a]						
1173w,sh [a]						
1108w,sh [a]						
	† 1094w					e_2 CD bend $\parallel$ (ν_{10})?
	† 1079m	† 1082	75	† 1082vvw [b]	† 1084m (*ca.* 0)	
	† 1066s	† 1069	180	† 1068w [b]	† 1073m (*ca.* 0)	
				† 1059m,sh [b]		
1057m,sp [a]	1056vs	1058	300	1051m,sp [b]	1059s (*ca.* 0)	a_1 ring breathing (ν_3)
1033w [a]				1031w-m [b]		
		1011	5			
988w [a]						
987w [a]				980vw [b]		a_2 CD bend $\parallel$ (ν_4)?
960vw,sh [a]				960vw [b]		
922w,sh [a]				916w-m [b]		
909w-m				906m [b]		
		858	8	853m,sh [c]		
853m [a]	851m	850	73	850m [c]	853m (0·73)	e_2 CD bend $\perp$ (ν_{11})
* 838vw [a]				* 832vw [c]		
779m-s [a]	774w-m	775	32	775w-m [c]		e_1 CD bend $\parallel$ (ν_6)
777sh [a]						
† 756w-m,sh [a]	759w-m	† 759	8	† 759w-m [c]		
† 753w-m [a]						
† 741w,sp [a]		† 741	16			
728m [a]	728m	727	59	720w,sh [c]		e_2 ring distortion $\parallel$ (ν_{13})
				710w,sh [c]		
694s [a]		692	21	685m-s [d]		e_1 CD bend $\perp$ (ν_7)
		689				
678m-s [a]						
670m-s [a]		670	4	663m-s [d]		a_1 Mn–C–O bend
		642				
629vs [a]		635	6	629vs [d]		e Mn–C–O bend
	623wv	620	9		618m,sh (*ca.* 0)	a_1 CD bend $\perp$ (ν_2)
609vs [a]	611w	609	55	608vs [d]	608m (*ca.* 0)	
563m [a]	564vw	562	9	558w [d]	560vw pol?	e_2 ring distortion $\perp$ (ν_{14})
545sh [a]	546w	545	42 } 77	540vs [d]	540w (0·75)	e Mn–C–O bend
539vs [a]	540w	535	35	529vs,sh [d]		
499sh [a]	500s	502	208		494s (*ca.* 0)	a_1 Mn–CO stretch
491m [a]	491m	488	116	488w	488m,sh dep?	e Mn–CO stretch
	361m	362	50			e_1 ring tilt
347w	346s,sh	351sh?		n.m.		
341vw,sh	340vs	340	1000	n.m.	337vs (*ca.* 0)	a_1 ring-Mn stretch
		132sh				
	117vs	118sh				
		111				
	99vs	98	3000		104vs (0·73)	OC–Mn–CO bends + ring-Mn–CO bends
		85				
		81				
		73				

Degree of depolarization given in parentheses. pol = Polarized. depol = Depolarized. n.m. = Not measured. * Residue bands of undeuteriated species. † Bands assigned to vibrations of partially deuteriated derivatives.

[a] From ref. 1. [b] Dissolved in CCl_4 (from ref. 1). [c] Dissolved in CS_2 (from refs. 1 and 2). [d] Dissolved in n-hexadecane (from ref. 1).

only fundamental of this class is in agreement with previous assignments. The band at 980 cm^{-1} in the i.r. spectrum of the deuteriated complex (H : D ratio 1·3) is tentatively assigned to this mode. The appearance of a band attributable to this formally inactive mode in both the i.r. and low-temperature Raman spectra is further evidence that the C_{5v} 'local' symmetry is only an approximation.

TABLE 3

Vibrational spectrum (cm^{-1}) of $[(\pi\text{-C}_5\text{H}_5)\text{Mo(CO)}_3]_2$

I.r. of CsI disc	I.r. of CCl$_4$ soln.	Raman of solid	Assignment
3125m,s,sh			a_1 CH stretch (ν_1)
3114m-s			e_1 CH stretch (ν_5)
3096w-m			e_2 CH stretch (ν_9)
		1999m	CO stretches
1962vs,sh	1960·5vs		
1952vs		1930w-m	
1923s-vs			
	1917vs		
	1911sh		
		1906m	
1900vs,r,sh			
1887vs			
		1868w-m	
1428m-s		1428w	e_1 CC stretch (ν_8)
1419m-s		1421w	
1358m		1359vw	e_2 CC stretch (ν_{12})
1350m			
1266w-m		1271vw	a_2 CH bend $\parallel$ (ν_4)
		(1220) *	e_2 CH bend $\parallel$ (ν_{10})
1185vw,br			(838 + 351)
1161vw,br			(823 + 337)
1106vw,sp		1107m-s	a_1 ring breathing (ν_3)
1068m		1069w	e_2 CH bend $\perp$ (ν_{11})
1058w			
1015m,sh			
1014m		1010w	e_1 CH bend $\parallel$ (ν_6)
1007w-m			
961vw,br			(547 + 415)
920w-m		924w	e_2 ring distortion $\parallel$ (ν_{13})
913m		918w	
851s			
838s-vs		832w-m,sh	e_1 CH bend $\perp$ (ν_7)
823vs		822w-m	a_1 CH bend $\perp$ (ν_2)
613w-m		610m-s	e_2 ring distortion $\perp$ (ν_{14})
606m			
		590m-s	Mo–C–O bends + Mo–CO stretches
587s-vs		560m	
547vs			
		540vw	
502s-vs		483m	
		483m	
477s			
		464s	
451vs			
		420m	
415m-s			
370w		366s	e_1 ring tilt
351m		345s,sh?	
337m		333vs	a_1 ring-Mo stretch
		113vs	OC–Mo–CO bends + ring-Mo–CO bends
		89vs	Mo–Mo stretch?
		81vs	
		73vs	

* Not observed; wavenumber estimated by comparison with the spectrum of the complex $(\pi\text{-C}_5\text{H}_5)\text{Mn(CO)}_3$.

e$_1$ *Class*. Most assignments of this class are straightforward. Bands observed at 3120, 3105, and 3095 cm^{-1} in the Raman spectrum of the sublimed solid must be formally associated with the e_1 and e_2 CH stretching modes (ν_5 and ν_9). Due to its strength in the i.r. spectrum the band at 3120 cm^{-1} is tentatively assigned to the e_1 mode (ν_5) and the remainder to the e_2 mode (ν_9).

The low intensity of the band at 1007 cm^{-1} in the Raman spectrum readily assigned to ν_6 is noteworthy, since, like other bands assigned to parallel bending modes, it is of low intensity compared with those assigned to the perpendicular bending modes. This may be used as an aid to assignment.

TABLE 4

Vibrational spectrum (cm^{-1}) of $[(\pi\text{-C}_5\text{D}_5)\text{Mo(CO)}_3]_2$

I.r. of CsI disc	Raman of solid	Assignment
* 3113w		
2356w,sh		a_1 CD stretch (ν_1)
2323m		e_1 CD stretch (ν_5)
2287w,sh		e_2 CD stretch (ν_9)
1960vs,sh		CO stretches
1950vs,sh		
1923s-vs		
1900vs,r,sh		
1887vs		
* 1427w		
* 1419w		
† 1365w-m		
† 1330w-m		
1318m-s		e_1 CC stretch (ν_8)
1303m-s		
1160w		
1106w,sp		
1090vw		
1048	1049m	a_1 ring breathing (ν_3)
1043 vw,sp		
1042		
* 1012w		
955w,br		
940w,br		
915w-m		
882w-m		
850m		e_2 CD bend $\perp$ (ν_{11})
* 823m-s		
778m		e_1 CD bend $\parallel$ (ν_6)
721w		e_2 ring distortion $\parallel$ (ν_{13})
701w		
680w		
662m		e_1 CD bend $\perp$ (ν_7)
636m,sh		
628m-s	625m	a_1 CD bend $\perp$ (ν_2)
* 607w		
	586m	Mo–C–O bends and/or Mo–CO stretches
580s-vs		
550vs	559m	
550vs		
537vs	536w-m	e_2 ring distortion $\perp$ (ν_{14}) + Mo–C–O bend or Mo–CO stretch
501vs		Mo–C–O bends and/or Mo–CO stretches
	483m	
477vs		
	468s	
450vs		
	422m	
414m-s		
375w-m	380w-m	
345w	344vs	e_1 ring tilt
† 337w		
322w-m	321vs	a_1 ring-Mo stretch
	113vvs	OC–Mo–CO bends—ring–Mo–CO bends
	89vvs	Mo–Mo stretch?
	84vvs	
	75vs,sh	

* Residue bands of undeuteriated species. † Bands assigned to vibrations of partially deuteriated derivatives.

e_2 *Class.* A band at *ca.* 1150 cm^{-1} in the i.r. spectrum has been previously assigned to the CH|| bend (ν_{10}),[1,3] but such an assignment is unlikely, since no band is observed in the Raman spectrum between 1220 and 1120 cm^{-1}. The very weak polarised band at 1220 cm^{-1} observed in the Raman only has, therefore, been assigned to ν_{10}. This is in agreement with the assignment of Adams and Squire.[4]

Since there is no evidence for the existence of a band at 1520 cm^{-1} in the Raman spectrum, the weak depolarised band at 1364 cm^{-1} clearly must be assigned to ν_{12}. This is in agreement with recent assignments [4-6,8] and is confirmed by the appearance of bands at 1256 and 1239 cm^{-1} in the Raman spectrum at 77 K and at 1260 cm^{-1} in the i.r. spectrum of the deuteriated derivative which are probable satellites of ν_{12} (H : D ratio 1·09). Bailey [7] has assigned a band at 1244 cm^{-1} to the equivalent mode of [$^2H_{10}$]ferrocene. A band at 909 cm^{-1} in the i.r. spectrum of (π-C_5D_5)Mn(CO)$_3$ has been assigned to ν_{13}. The absence of this band in the Raman spectrum makes this assignment doubtful. However, a medium intensity band at 728 cm^{-1} in the Raman spectrum remains unassigned and could be associated with ν_{13}. The very weak band at 1011 cm^{-1} in the low temperature solid Raman spectrum of the deuteriated derivative is a possible satellite of ν_{10} (H : D ratio 1·20). However, such an assignment gives a product rule ratio of 0·30 which is considerably less than the theoretical 0·354. This would imply, assuming all other assignments to be correct, that ν_{10} of the deuteriated derivative should be at a higher frequency. A band at 1084 cm^{-1} assigned to ring breathing of a partially deuteriated derivative could be also assigned to ν_{10} and this would give a product rule ratio of 0·354. Such an assignment would give a H : D ratio of 1·115 rather low for a CH|| bend, but comparable to the ratio of 1·125 for the equivalent mode of ferrocene.[7]

One feature of the spectrum of (π-C_5D_5)Mn(CO)$_3$ requires some explanation. The weak polarised Raman band at 667 cm^{-1}, which is strong in the i.r., loses considerable intensity in both cases on deuteriation, but the band has been previously reasonably assigned as a Mn–C–O bending mode.[2-4] The band is unlikely to be a ring mode, since no band is observed within 50 cm^{-1} in the i.r. spectra of eleven other (π-cyclopentadienyl)-metal carbonyls.[1,2] The following explanation is suggested, that the previous assignment is correct but, the band loses intensity by interaction with the CD$\perp$ bend (ν_7) at 685 cm^{-1}, the latter band gaining intensity as a consequence.

(ii) *Carbonyl stretching vibrations.* According to the 'local' symmetry approach, the symmetry of the Mn(CO)$_3$ moiety should be C_{3v}. This is shown to be true in solution by the appearance of two bands attributable to ν(CO) modes. Polarisation characteristics of these readily identify the 2027 cm^{-1} as the a_1 mode and that at 1944 cm^{-1} as the e mode. This confirms previous assignments.[3,4]

(iii) *Low frequency vibrations* (*below* 700 *cm*$^{-1}$). Several types of vibration are expected to occur below 700 cm^{-1}, *viz*: ν_{14}, Mn–C–O bending modes [δ(Mn–C–O)], Mn–CO stretching modes [ν(Mn–CO)], M–C_5H_5 stretching modes, OC–Mn–CO bending modes [δ(C–Mn–C)] and OC–Mn–C_5H_5 bending modes [δ(OC–Mn–C_5H_5)].

Bands *ca.* 100 cm^{-1} may be readily assigned to δ(C–Mn–C) and δ(OC–Mn–C_5H_5) modes although it is not possible to distinguish the individual vibrations. The main depolarised band may, however, be tentatively assigned to the e δ(C–Mn–C).

The very strong polarised band at 348 and 337 cm^{-1} in the Raman spectrum of complex and its deuteriated derivative respectively are readily assigned to the a_1 ring–metal stretch (H : D ratio 1·03), while the depolarised band at 372 cm^{-1} in the Raman spectrum of the complex must be the e_1 ring–metal stretch (the ring tilt). This confirms previous assignments.

The assignment of bands to the δ(Mn–C–O) and ν(Mn–CO) modes is more complex. Previously,[2] from its i.r. spectrum, the incomplete Raman data of Lippincott *et al.*,[3] and the i.r. spectra of certain substituted derivatives of the types (π-C_5H_5)Mn(CO)$_2$L and (π-C_5H_5)Mn(CO)L$_2$ [2] the following assignments were made, *viz*: 666 and 635 cm^{-1} to e δ(Mn–C–O), 611 cm^{-1} to ν_{14}, 541 cm^{-1} to a_1 δ(Mn–C–O), 500 cm^{-1} to a_1 ν(Mn–CO), and 494 cm^{-1} to e ν(Mn–CO). The last two assignments are clearly correct from their intensity, band position, and polarisation characteristics in the Raman spectrum, while the assignment of the 541 cm^{-1} band to an a_1 mode must be incorrect as the band is depolarised. The 541 cm^{-1} band must, therefore, be assigned to an e δ(Mn–C–O) mode, as must the 635 cm^{-1} band, which is very strong in the i.r. spectrum and very weak in the Raman. These assignments are in agreement with those of Adams and Squire.[4] It has been noted in the above discussions, that bending vibrations perpendicular to the plane of the ring (*i.e.* parallel to the plane of symmetry of the whole molecule) are of higher intensity in the Raman spectrum than those bending vibrations parallel to the plane of the ring (*i.e.* perpendicular to the plane of symmetry of the whole molecule). It is, therefore, reasonable to infer that the band at 541 cm^{-1} is associated with a δ(Mn–C–O) mode which vibrates parallel to the plane of symmetry of the molecule, while that at 635 cm^{-1} does so perpendicular to the plane of symmetry. There remains to be assigned one a_1 and one a_2 δ(Mn–C–O) mode. It is unlikely that the latter mode which is both i.r. and Raman inactive will be observed. The bands at 667 and 611 cm^{-1} in the Raman spectrum are both polarised and either could be assigned to the a_1 mode. The band at 611 cm^{-1} has already been assigned to ν_{14} by comparison with the i.r. spectra of a number of other (π-cyclopentadienyl)metal carbonyls, therefore, the 667 cm^{-1} band is assigned to the a_1 δ(Mn–C–O) mode as noted above.

Effect of Change of State on the Spectrum of (π-C_5H_5)Mn(CO)$_3$.—Since (π-C_5H_5)Mn(CO)$_3$ is a low melting (350 K), readily vacuum sublimable solid, it is possible to examine its vibrational spectrum in the solid, liquid, and gaseous states. In the solid state its spectrum has been examined at room and liquid-nitrogen temperatures. It was, however, not possible to measure the gas-phase Raman spectrum of the complex due to rapid decomposition which occurred even when the laser beam had been drastically detuned. The complex is also sufficiently soluble in both CCl_4 and CS_2 to enable its spectrum to be measured in solution.

(a) *Ring vibrations.* Previously,[1] it was noted that, in solution, the part of the i.r. spectrum associated with ring vibrations could be interpreted on a symmetry very close to that of the 'local' symmetry C_{5v} expected for the C_5H_5–Mn moiety. The evidence for this is that bands assigned to the strictly i.r.-active a_2 and e_2 modes were only observed weakly at 1267 cm^{-1}, a doublet centred at 1055 and at 922 cm^{-1}. The close approach to the 'local' symmetry is confirmed by the polarisation characteristics of bands in the solution Raman spectrum, discussed above. As expected, the liquid spectrum very closely resembles that in solution, although there is evidence from the i.r. spectrum of an even closer approach to C_{5v} symmetry, since no band attributable to ν_{12} is observed. In the gas phase i.r. spectrum, the only evidence for breakdown of C_{5v} selection rules is seen in the very weak band at 1256 cm^{-1} and the very weak shoulder at 1038 cm^{-1}.

Clearly, from the above evidence, there must be little interaction between the modes of the π-cyclopentadienyl–metal and metal–carbonyl moieties in the gas-phase spectrum of the complex, which may be explained by the ability of the ring freely to rotate under these conditions. This implies that $(\pi\text{-}C_5H_5)Mn(CO)_3$ exists as individual molecules in the gas phase with little interaction between them. A further breakdown of the selection rules for C_{5v} in the liquid phase is indicative of the expected increased interaction between the $(\pi\text{-}C_5H_5)Mn(CO)_3$ molecules and consequent decreased ease of rotation of the ring. However differences between the gas- and liquid-phase spectra are small, which shows that even in the liquid phase interaction between the molecules is weak. The slight difference between liquid and solution i.r. spectra may be explained by small specific solvent–solute interactions.

The solid spectrum must be interpreted in the light of its crystal structure. Berndt and Marsh [10] found that the complex crystallises in the $P2_1/a$ (C_{2h}) space group with four molecules in the unit cell. Halford [11] has shown that the site symmetries for this space group are $4C_i(2)$. A site symmetry of C_i cannot be appropriate to the $\pi\text{-}C_5H_5$–Mn moiety, since C_i is not a sub-group of C_{5v}; a trivial site symmetry of C_1 must, therefore, be proposed for this moiety. The selection rules for this molecular point group dictate that all modes are non-degenerate and both i.r. and Raman active. Examination of the solid spectrum reveals that all bands associated with degenerate modes, are split, notably those associated with e_2 modes, and that the band associated with the a_2 mode is only observed in the Raman spectrum at 77 K. There is no suitable point symmetry for the moiety that would explain such observations and, therefore, the solid spectrum may only be explained in trivial terms. It is, therefore, suggested that in the solid state interaction occurs between the $\pi\text{-}C_5H_5$–Mn and $Mn(CO)_3$ moieties so that the 'local' symmetry approach is no longer applicable. This interaction is clearly illustrated by the behaviour of bands assigned to the ring tilting mode which involves both moieties. In the solution Raman spectrum, this e_1 mode appears as a weak shoulder at 372 cm^{-1}, whereas in the solid spectrum two bands of medium to strong intensity are observed separated by 20 cm^{-1}. Interaction between the moieties probably occurs due to the lack of rotation of the π-cyclopentadienyl ring and the spectrum is, therefore, best interpreted by assuming a symmetry approaching C_s, which is the greatest overall symmetry possible for the molecule.

Comparison of the Raman spectrum of the complex at room and liquid nitrogen temperatures reveals that the intensity of the bands assigned to e_1 and e_2 modes rise compared to those assigned to a_1 modes, while the band attributed to the a_2 mode is observed, as the temperature is lowered. This supports the idea, that as the temperature falls, the π-cyclopentadienyl ring is able to rotate less readily, and hence the symmetry of the $\pi\text{-}C_5H_5$–Mn moiety is lowered giving increasing symmetric character to a_2, e_1, and e_2 modes and thus increasing their intensity. Also, as expected, the splitting of bands associated with e_1 and e_2 modes is greater as the temperature is lowered. The increased intensity and splitting of bands assigned to e_1 and e_2 modes is further confirmation of their correct assignment.

(b) CO *Stretching vibrations.* The vibrational spectrum of the complex in the CO stretching region, in the gaseous and liquid states as well as in solution, may be readily interpreted using a 'local' C_{3v} symmetry for the $Mn(CO)_3$ moiety. This supports the idea that there is little interaction between the $\pi\text{-}C_5H_5$–Mn and $Mn(CO)_3$ moieties under these conditions. There is, however, a dramatic change in the spectrum in the solid state. The solid spectrum in this region has recently been studied with those of related complexes by Kettle *et al.*[12] and been intrepreted by formal factor-group analysis, using a C_{2h} isomeric point symmetry group, which predicts six i.r. and six Raman active non-coincident ν(CO) modes. The results reported here are in essential agreement with their work except that no shoulder was observed at 1936 cm^{-1} in the Raman spectrum.

(c) ν(Mn–CO) *Vibrations.* As expected for the C_{3v} 'local' symmetry two bands *ca.* 500 and 495 cm^{-1} are observed in the gaseous, liquid, and solution spectra. It might be expected that, since between four and six bands have been observed in the solid state spectra in the CO stretching region, a similar number of bands might be observed *ca.* 500 cm^{-1}. However, the Raman

---

[10] A. F. Berndt and R. E. Marsh, *Acta Cryst.*, 1963, **16**, 118.

[11] R. S. Halford, *J. Chem. Phys.*, 1946, **14**, 8.

[12] H. J. Buttery, S. F. A. Kettle, G. Keeling, P. J. Stamper, and I. Paul, *J. Chem. Soc. (A)*, 1971, 3148.

spectrum of the solid, even at 77 K, only reveals two bands attributable to ν(Mn–CO) vibrations. This may be explained by the close proximity of the bands and the low resolution of the instrument caused by the wide slits necessary to obtain the spectrum. However, the low-temperature i.r. spectrum of the complex does have two additional shoulders compared with the solution spectrum.

(d) δ(Mn–C–O) *Vibrations.* As expected for the C_{3v} symmetry three bands attributable to δ(Mn–C–O) are observed in the gas, liquid, and solution spectra. In the solid state factor-group analysis predicts 24 active modes, 12 i.r. ($6a_u + 6b_u$) and 12 Raman ($6a_g + 6b_g$), based on the isomorphic point symmetry of C_{2h}.[13] The low number of observed bands is probably due to their close proximity in the spectrum.

(e) δ(C–Mn–C) *and* δ(OC–Mn–C_5H_5) *Vibrations.* The considerable splitting of the bands in the 100 cm^{-1} region on solidification is further evidence for the interaction between modes of the π-C_5H_5–Mn and Mn$(CO)_3$ moieties in the solid state. However, splitting may be enhanced by mixing of these vibrations with lattice vibrations.

Band Assignment for Bis[tricarbonyl(π-cyclopentadienyl)molybdenum] and its Deuteriated Derivative.—(i) *π-Cyclopentadienyl ring vibrations.* Assignments are given in the Tables. Examination of the vibrational spectra of [(π-C_5H_5)Mo$(CO)_3$]$_2$ and [(π-C_5D_5)Mo$(CO)_3$]$_2$ supports the assignments made for ring modes of the manganese complex. The observed product ratio of 0·526 for the a_1 class is in good agreement with the theoretical 0·509. No calculation was carried out for the e_2 class, since no band attributable to ν_{10} was observed.

Previously,[1] no band was assigned to ν_{14} in the i.r. spectrum of [(π-C_5D_5)Mo$(CO)_3$]$_2$ as it was assumed that it would be masked by vibrations of the Mo$(CO)_3$ moiety. However, a band was observed at 539 cm^{-1} in the spectrum, which was clearly a ring mode, but was not assigned. Comparison of the Raman spectrum of the molybdenum complex and its deuteriated derivative, however, indicates that the 539 cm^{-1} band is a probable satellite of the 608 cm^{-1} band (H : D ratio 1·13).

Although assignments have been made on the basis of a C_{5v} ' local ' symmetry, it is clear from the spectrum that, as with the solid spectrum of (π-C_5H_5)Mn$(CO)_3$, this symmetry is not an adequate approximation. As previously noted,[1] band splittings indicate a lower symmetry for the π-C_5H_5–Mo moiety of this complex than for the π-C_5H_5–Mn moiety of (π-C_5H_5)Mn$(CO)_3$.

(ii) *Carbonyl stretching vibrations.* The vibrational spectrum in the CO stretching region for this complex is not easily interpreted. However, since there are no coincidences in the solid state i.r. and Raman spectra, it is clear that the overall crystal symmetry must be centrosymmetric. The crystal structure[14] indicates that the point symmetry of the molecule approaches C_{2h} and, therefore, three bands are expected in both the solution i.r. ($a_u + 2b_u$) and Raman ($2a_g + b_g$). The three expected bands are observed in the i.r. spectrum, but unfortunately because of decomposition of the sample solution in the laser beam no Raman spectrum could be obtained.

(iii) *Low-frequency vibrations.* Bands *ca.* 100 cm^{-1} may be readily assigned to δ(C–Mo–C) and δ(OC–Mo–C_5H_5) modes, whereas those at 89 and 81 cm^{-1}, much stronger than any in this region for the Mn complex, may be due to ν(Mo–Mo). It is likely that there is mixing of the modes with lattice vibrations.

The very strong band, in the Raman spectrum, at 333 cm^{-1}, which is found at 321 cm^{-1} in the spectrum of its deuteriated derivative, is readily assigned to the a_1 ring–metal stretch (H : D ratio 1·04). The band at 366 removed to 344 cm^{-1} in that of the deuteriated derivative must be assigned to the e_1 ring–metal stretch (the ring tilt) an H : D ratio of 1·07. The band at 610 removed to 537 cm^{-1} in the spectrum of its deuteriated derivative has already been assigned to ν_{14}.

At least six non-coincident bands are found in the range 600—400 cm^{-1} in the i.r. and Raman spectrum of the complex, measured in the solid state, which must be assigned to δ(Mo–C–O) and ν(Mo–CO) modes. This confirms the centrosymmetric nature of the crystal symmetry. Clearly assignment of bands to these modes is not possible for such a complex system, but it is likely that the very strong band in the Raman spectrum at 464 cm^{-1} is associated with an a_g ν(Mo–CO) mode.

EXPERIMENTAL

The complexes (π-C_5H_5)Mn$(CO)_3$ and [(π-C_5H_5)Mo$(CO)_3$]$_2$ were obtained from Alpha Inorganics (π-C_5H_5)Mn$(CO)_3$ was resublimed before use. The deuteriated samples of the complexes were prepared as previously described [1] and were estimated to be approximately 80% deuteriated for the Mn complex and 70% for the Mo complex.

Infrared Spectra.—Spectra in the region 3500—200 cm^{-1} were recorded on the Perkin-Elmer 225 spectrophotometer and calibrated with polystyrene and indene. Band positions should be accurate to at least ±2 cm^{-1}. Spectra of solutions in the range 3500—400 cm^{-1} were measured using a compensated variable path length cell with KBr windows and those in the range 400—200 cm^{-1} using an uncompensated cell with CsI windows. CsI discs were prepared using spectroscopic grade CsI. The gas phase spectrum was measured using an evacuated 10 cm heated gas cell with KBr windows. The liquid spectrum was measured using an R.I.I.C. variable temperature i.r. unit with silver chloride windows fitted with a jacket with KBr windows by the following method.

Some powdered (π-C_5H_5)Mn$(CO)_3$ was placed between the silver chloride plates together with a suitable spacer. The unit was then heated using the automatic temperature controller to 353 K, just above the m.p. of the complex, when the unit was placed in the sample chamber of the spectrophotometer and the spectrum measured. The spectrum of the solid film was obtained in a similar way. The solid sample was again heated in the unit to 353 K, whereupon it was rapidly cooled by addition of liquid

---

[13] D. M. Adams, personal communication.

[14] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

nitrogen to form a solid film at *ca.* 77 K. To prevent fogging of the jacket windows, these were heated to above room temperature.

Raman Spectra.—Spectra were recorded using a Spex 1401 spectrometer in conjunction with a Coherent Radiation 52 krypton ion laser. The scattered radiation was collected at 90° and focused by an *f*/0·95 lens on to the entrance slit of the monochromator after having passed through a polarisation scrambler. The 0·75 m Czerny–Turner monochromator employed two 1200 lines mm^{-1} Baush and Lomb gratings blazed at 500 nm. The method of detection was photon counting (cooled FW 130 phototube). The exciting lines were those at 647·1 (Mn and Mo complexes) and 568·2 nm [$(\pi\text{-}C_5H_5)Mn(CO)_3$ only]. The maximum power available with these lines was 750 and 300 mW respectively, although, in general, it was found necessary to record the spectra of the compounds at lower powers. For measurement of the spectra of the Mo complex and its deuteriated derivative it was found necessary to remove the focusing lens of the sample illuminator, as described elsewhere,[15] in order to prevent decomposition of the sample through local heating. Solid spectra at room temperature were measured using samples held in a metal probe. Solid films were prepared by sublimation of the sample *in vacuo* on to a glass cold-finger cooled by liquid nitrogen and their spectra measured at *ca.* 77 K using the cell described elsewhere.[16] Solution spectra were measured with the sample in a capillary tube. Spectra in the liquid state were measured on samples in sealed (Pyrex or silica) ampoules heated in a furnace.[17] The spectra were calibrated by reference to the emission lines of neon and band positions should be accurate to at least ±2 cm^{-1}.

Depolarisation ratios were obtained from the ratio of the masses of traces of the bands obtained with the analyser in the perpendicular and parallel positions. The maximum ρ value is $\frac{3}{4}$.

Comparative intensity measurements were obtained by weighing traces of the bands and relating their masses to the mass of the strongest simple band in the spectrum, correcting for changes in instrument response with frequency.

The author wishes to thank Dr. R. J. H. Clark for provision of i.r. and Raman facilities, Mr. Peter Mitchell for technical advice and for running the Raman spectra, and Dr. D. M. Adams for helpful discussions.

[3/766 *Received*, 10*th April*, 1973]

---

[15] R. J. H. Clark, B. K. Hunter, and P. D. Mitchell, *J.C.S. Faraday II*, 1972, 476.

[16] R. J. H. Clark and B. K. Hunter, *J. Chem. Soc.* (*A*), 1971, 2999.

[17] R. J. H. Clark, B. K. Hunter, and D. M. Rippon, *Inorg. Chem.*, 1972, **11**, 56.