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A COMPARATIVE STUDY OF THE VIBRATIONAL SPECTRA OF (π-PYRROLYL)TRICARBONYLMANGANESE AND (π-CYCLOPENTADIENYL)TRICARBONYLMANGANESE

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Summary

Infrared and Raman spectra of (π-C_4H_4N)Mn$(CO)_3$ and IR spectra of (π-C_4D_4)Mn$(CO)_3$ have been studied, and an assignment of the vibrational frequencies has been made. The frequencies of C_4H_4N ligand closely resemble those of the C_5H_5 ring in (π-C_5H_5)Mn$(CO)_3$. The replacement of the CH group by nitrogen scarcely affects the mechanical properties of the ring. In spite of the lowering of local symmetry of the ligand from C_{5v} to C_s, splitting of the degenerate modes was not observed. However, the modes, active only in the Raman spectrum for the Cp-ring, for the pyrrolyl ligand also appear in the IR spectrum. On the basis of comparison of the spectra of PTM and CTM and the new investigation of Raman spectra of CTM, a reassignment of some CTM vibrational modes is offered.

Introduction

π-Pyrrolyl complexes of transition metals are analogous to the corresponding π-cyclopentadienyl derivatives. IR spectra of the pyrrolyl anion, azaferrocene [1] and (π-pyrrolyl)tricarbonylmanganese (PTM) [2] show that the frequencies of the pyrrolyl ring closely resemble those of the cyclopentadienyl ring: The replacement of the CH group in the ring by nitrogen has little effect on the ring vibrations. The additional IR bands for pyrrolyl derivatives in comparison with cyclopentadienyl compounds correspond to the Raman bands of the latter and appear in the IR spectrum due to decrease in molecular symmetry. It was noted [1] on the base of the selection rules that the symmetry of the $C_4H_4N^-$ anion is more nearly D_{5h} than C_{2v}. The Raman spectra of π-pyrrolyl complexes was not investigated.

It is of interest to carry out more detailed study of vibrational spectra of π-pyrrolyl complexes and to compare them with the data for π-cyclopentadienyl compounds in order to determine the heteroatom influence on spectral characteristics of the complex. In this work the IR and Raman spectra of PTM and PTM-d_4 are studied, assignment is offered and the data are compared with those for (π-cyclopentadienyl)tricarbonylmanganese (CTM). For CTM assignment of the normal modes has already been proposed [4], but comparison of the data for PTM and CTM and the reinvestigation of the Raman spectra of CTM lead us to propose a new assignment for several vibrational frequencies.

Experimental

IR spectra were run on FIS-1, Zeiss UR-20 and Perkin—Elmer 457 instruments as KBr discs, nujol mulls and solutions in CS_2 and CH_2Cl_2. Raman spectra of PTM were obtained on a Coderg PHO Raman-laser spectrometer with the He/Ne laser exitation (6328 Å) for solid samples (in sealed tubes under argon) and in CH_2Cl_2 solutions. All the solutions were prepared under argon, since in

TABLE 1

PTM AND PTM-d_4 VIBRATIONAL FREQUENCIES (cm^{-1})

PTM				PTM-d_4	Assignment
IR		Raman		IR	
Solid	Solution	Solid	Solution	Solution	
		3138w			
3129m	3122vw				
3113(sh)		3117vw			
	3103vw	3103m			
3087w		3090w			
2040vs	2038vs	2036m	2038s,P		ν(CO) (A_1)
		1970m			
1952vs	1953vs	1959m	1955m		ν(CO) (E)
		1939w			
		1926w			
1411m	1410m	1420w		1325	ν(CC) (E_1)
1363	1360m	1368w		1210	ν(CC) (E_2)
1277m	1277m			1125	δ(CH) (A_2)
1265(sh)					
1193m	1197m			895	δ(CH) (E_2)
1117w	1117w	1119s	1120s,P	1070	ν(ring) (A_1)
1078m	1074m	1085w		850(870)	ρ(CH) (E_2)
1070m					
1050(sh)	1047w	1039w			
1029(sh)	1027(sh)				
1012s		1018w		795	δ(CH) (E_1)
	968vw				
920m	904w-m			870(743)	δ(CC) (E_2)
866s	863s	858w		683	ρ(CH) (E_1)
853s	837s				ρ(CH) (A_1)
670s	667s			590	χ(CC) (E_2)
657m	652m			652	δ(MnCO) (A_1)
634s	633s			633s	δ(MnCO) (E)
546(sh)		545vw			
535s	535s			535s	δ(MnCO) (E)
492w		498w	500s,P		ν(Mn—CO) (A_1)
		487(sh)			ν(Mn—CO) (E)
384w		380s	380w		ν(MnC) (E_1)
375m			366m		
		347vs	342vs,P		ν(MnC) (A_1)
			100m		δ(CMnC)

TABLE 2

VIBRATIONAL SPECTRA OF CTM IN SOLUTION (cm^{-1})

Infrared[a]	Raman[b]	Assignment[c]
	3123m,P	ν(CH) (A_1)
3115w		
	3102w	ν(CH) (E_1,E_2)
2025vs	2020m,P	ν(CO) (A_1)
1038vs	1032s	ν(CO) (E)
1427m	1427m	ν(CC) (E_1)
1360w	1364w	ν(CC) (E_2)
1265w		δ(CH) (A_2)
1202w	1216w,P	δ(CH) (E_2)
1152vw		
1113m	1116vs,P	ν(ring) (A_1)
1062m	1063s	ρ(CH) (E_2)
1050m		
1010s	1010w	δ(CH) (E_1)
920w	930w	δ(CC) (E_2)
905w		
850(sh)	845(sh)	ρ(CH) (E_1)
831s	837s,P	ρ(CH) (A_1)
667s	670m,P	δ(MnCO) (A_1)
635vs	635w	δ(MnCo) (E)
	608m,P?	χ(CC) (E_2)
542s	540m	δ(MnCO) (E)
	500s,P	ν(MnCO) (A_1)
490w	493(sh)	ν(MnCO) (E)
	380(sh)	ν(MnCp) (E_1)
	353vs,P	ν(MnCp) (E_1)
	104	δ(CMnC)

[a] Solutions in CS_2, CH_2Cl_2. [b] Solutions in CH_2Cl_2, CH_3I, CCl_4. [c] The assignment is based on local symmetry C_{5v} of the MnCp moiety, and C_{3v} of the $Mn(CO)_3$ moiety.

air rapid decomposition takes place. PTM was obtained by a previously described method [2]. Raman spectra of CTM were obtained for CH_2Cl_2, CH_3I and CCl_4 solutions. PTM-d_4 was obtained by the method described in ref. 3. The sample contained (mass spectral data) 53% of PTM-d_4, 41% of PTM, 3% of PTM-d_1, 1% of PTM-d_2 and 2% of PTM-d_3. The IR spectrum of PTM-d_4 in CS_2 solution was referenced against a PTM solution.

Results and discussion

The spectra are presented in Tables 1 and 2. The assignment is facilitated by comparison of the spectra of PTM and PTM-d_4 with those of CTM [4], (π-cyclopentadienyl)tricarbonylrhenium (CTR) [5] and benzenetricarbonylchromium [6,7]. In Table 3 the frequencies of PTM and PTM-d_4 are compared with the corresponding frequencies of CTM and CTM-d_5. The assignment is discussed below.

The vibrational frequencies of PTM and CTM and their shifts under deuteration are very similar; both have the same symmetry C_s. But it is assumed that there is a little interaction between the ring and $M(CO)_3$ vibrations, and so the method of "local symmetry" is applicable. For CTM the vibrations can be described on the basis of C_{5v} symmetry for the metal—ring moiety and C_{3v} symmetry for $M(CO)_3$ moiety [4]. Some IR-forbidden bands for C_{5v} symmetry (A_2 and E_2) were observed for CTM as weak bands due to the decrease of symmetry under the influence of the $M(CO)_3$ group. For PTM the local symmetry of the metal—ring moiety is C_S and the C_{5v} symmetry-forbidden bands appear in the IR spectrum. This sometimes helps to corroborate the CTM assignments.

1. *Pyrrolyl ligand modes*

For the C_4H_4N ring with local symmetry C_S 21 normal modes are expected ($11A'$ and $10A''$).

(a). Ring modes. For the C_5H_5 ring with C_{5v} symmetry 3 C—C stretching modes are expected ($A_1 + E_1 + E_2$). To the ring breathing vibration (A_1) the strong polarized line 1120 cm^{-1} in the CTM Raman spectrum has been assigned. For PTM this band was observed at 1117 cm^{-1} in the IR and at 1119 cm^{-1} in the Raman, and shifts to 1070 cm^{-1} under deuteration. The E_1 band was observed for CTM at 1427 cm^{-1} and for PTM at 1410 cm^{-1} (1325 cm^{-1} for PTM-d_4). The assignment of the infrared inactive E_2 mode has been previously discussed, and for CTM the weak IR band at 1525 cm^{-1} was assigned to it [4]. However it was later shown [5] for C_5H_5 derivatives that this mode more likely corresponds to the frequency at about 1360 cm^{-1}, weak in the Raman spectra and observed, sometimes, in the IR spectra due to lowering of the local symmetry on due to crystal effects. This band was found for CTR [5], ferrocene [8], ruthenocene [9] and other C_5H_5 compounds. In the Raman spectrum of CTM, obtained by us, the depolarized line at 1364 cm^{-1} was observed and no line in the 1520 cm^{-1} region was found. In the PTM spectrum the medium intensity IR band at 1360 cm^{-1} was observed. The appearance of this band for PTM, taking into account the resemblance of PTM and CTM frequencies, is indirect evidence that this is one

TABLE 3

π-LIGAND VIBRATIONAL FREQUENCIES (cm^{-1}) IN PTM, CTM[a] AND THEIR DEUTERATED DERIVATIVES (C_{5v} LOCAL SYMMETRY)

	PTM	PTM-d_4	CTM	CTM-d_5	Symmetry
ν(CH) or ν(CD)	3135		3125	2345	A_1
	3127				
	3111			2345	E_1
	3087		3096		E_2
δ(CH) or δ(CD)	1277	1125	1266	983	A_2
	1011	795	1014	779	E_1
	1197	895	1154 (1216)	909	E_2
ρ(CH) or ρ(CD)	837		837	609	A_1
	863	683	848	694	E_1
	1074	850	1064	853	E_2
ν(CC)	1117	1070	1114	1057	A_1
	1410	1325	1424	1313	E_1
	1368	1210	1360	1230	E_2
δ(CC)	904	870(743)	941	909	E_2
χ(CC)	667	590	611	563	E_2

[a] Values for CTM and CTM-d_4 are taken from ref. 11, although some assignments are changed.

of the fundamental modes for C_5H_5 derivatives. After deuteration the band shifts to 1210 cm^{-1}. The value of the shift [$\nu(H)/\nu(D) = 1.12$] is somewhat larger than expected for a ring mode, but this may be due to the participation of the CCH angle deformation in this vibration [10]. The splitting of the E_1 and E_2 modes on the lowering of the ligand symmetry from C_{5v} to C_S for the pyrrolyl ring can be expected. However, for PTM this splitting was not observed, i.e. the pyrrolyl ring vibrations can be described in terms of C_{5v} symmetry. Therefore the introduction of the nitrogen atom to the ring in place of the CH group hardly change its mecanical properties (the mass of nitrogen is similar to the CH group mass, and the force constants of C—C and C—N bonds are similar also). This is reflected also in the similarity of the C_5H_5 and C_4H_4N ring frequencies and in the conservation of the frequency degeneration. But from the electro-optical point of view the C—C and C—N bonds are not equivalent (the different values of dipole moment derivatives and polarizability derivatives with respect to vibrational coordinates). Thus the selection rules for intensities correspond to C_S symmetry but not to C_{5v}.

To the in-plane bending modes of the ring (E_2) the freqeuncies at 900, 920, 935 cm^{-1} were assigned for ferrocene, CTM and CTR respectively. In the spectra of PTM we assign to this mode the IR band 920 cm^{-1} (for the solid), which shifts to 904 cm^{-1} in CS_2 solution. For PTM-d_4 the assignment of this band is not clear. It has been suggested that for CTM this band shifts from 941 cm^{-1} to 909 cm^{-1} for CTM-d_5 [$\nu(H)/\nu(D) = 1.03$][10]. But for ferrocene it is proposed that the band shifts from 892 cm^{-1} to 743 or 706 cm^{-1} for ferrocene-d_{10} [$\nu(H)/\nu(D) = 1.20$—1.26] and such a large shift can be explained by the participation of the CCH angle deformations in the mode.For PTM-d_4 it is possible to assign to the δ(ring) (E_2) mode the band 870 cm^{-1} [$\nu(H)/\nu(D) = 1.04$] or 743 cm^{-1} [$\nu(H)/\nu(D) = 1.22$].

To the put-of-plane C_5H_5 ring mode (E_2) the band at 600 cm^{-1} was assigned for ferrocene (552 cm^{-1} for ferrocene-d_{10})[15]. The very weak IR band at 489 cm^{-1} has been assigned to this mode of CTM [14] and the weak 609 cm^{-1} IR band, found only for the solid state and not observed in Raman, was assigned to the forbidden A_2 MCO bending mode. But in later work [11], the latter band was assigned to χ(ring) (E_2) mode, taking into account its shift to 563 cm^{-1} under deuteration. It seems to us that this assignment is preferable. First, it accords better with the assignments for other C_5H_5 derivatives. Secondly, for CTM in CCl_4 solution we have observed the Raman band at 608 cm^{-1} with the intensity similar to the intensities of the neighbouring δ(MCO) modes. Thirdly, in the PTM IR spectrum there is the band in the same region at 667 cm^{-1}, which shifts to 590 $cm^{-1}$for PTM-d_4. The large shift [$\nu(H)/\nu(D) = 1.13$] can be explained by the participation of out-of-plane CH deformations in the mode, which is suggested by calculation data [10].

(b). In-plane CH bending modes. For the Cp-ring (C_{5v}), three δ(CH) modes are expected ($A_2 + E_1 + E_2$). Only E_1 is IR-active; A_2 is IR- and Raman-forbidden and appears as a rule only in the crystal spectra. In Raman, $E_1$and E_2 are allowed, but weak. The majority of authors assign to the E_1 vibration the strong band near 1000 cm^{-1} , observed in the IR spectra of all Cp-compounds. Its assignment to out-of-plane CH modes for $CpW(CO)_3CH_3$ [12] is very doubtful, because it is in contradiction with the data on other Cp-derivatives. For example, the envelope of this band in the IR gas spectrum of CpNiNO [13] gives evidence of its in-plane nature. The isotopic shift to 800 cm^{-1} under deuteration suggests that this mode is a CH vibration. In the PTM spectra the corresponding band is at 1011 cm^{-1}

(795 cm^{-1} for PTM-d_4). The position of the PTM IR band at 1277 cm^{-1} coincides with the positions of the weak bands, usually assigned for Cp-compounds to A_2 mode (1250 cm^{-1} for Cp_2Fe, 1266 cm^{-1} for CTM). The δ(CH) (E_2) modes in Cp-compounds are in the 1150-1190 cm^{-1} region (near 900 cm^{-1} in deuterated derivatives) [11]. The weak IR band at 1152 cm^{-1} of CTM was assigned to this mode [4,11]. We could not find this line in the Raman spectrum of CTM, but in this region the line 1216 cm^{-1} has been observed. Unexpectedly this line is polarized (CH_2Cl_2, CH_3I solutions). The line at 1185 cm^{-1} in the Raman spectrum of ferrocene, assigned to δ(CH) (E_2) [8,14], as we have discovered, is polarized also. The intensities of these Raman lines are of the same order as the lines of the other degenerate modes. This fact and also the appearance in the PTM IR spectrum of the 1197 cm^{-1} band (895 cm^{-1} in PTM-d_4) allow us to suppose that all these bands belong to the fundamental modes. The polarization of the line for CTM can be explained by the lowering of the local symmetry of the ring under the influence of the $M(CO)_3$ moiety, by the corresponding splitting of E_2 mode to A' and A'' (C_S symmetry) and by the predominant appearance in the Raman spectrum only of the symmetrical component. But this explanation is not satisfactory for Cp_2Fe; additional study is needed.

The pyrrolyl ring contains only 4 C—H bonds and has the C_s local symmetry Four δ(CH) ($2A' + 2A''$) modes are expected. Three of them are in the same regions as for the corresponding Cp-derivatives. The fourth band, probably, is the weak band at 1020 cm^{-1}, observed as a shoulder at 1011 cm^{-1} band in the solid and solution IR spectra.

(c). Out-of-plane CH bending modes. The PTM IR bands at 837, 863 and 1074 cm^{-1} are located in the same regions as the bands, usually assigned to out-of-plane CH modes of cyclopentatienyl compounds ($A_1 + E_1 \pm E_2$). The last band for Cp-derivatives is weak or absent in the IR, but in the Raman this mode is characterized by an intense line, which must be assigned to the E_2 mode. For PTM this mode is IR-active. The 863 and 1074 cm^{-1} bands shift to 683 and 850 cm^{-1} respectively under deuteration. The band of PTM-d_4, corresponding to the PTM band at 837 cm^{-1}, was not observed, probably due to overlapping with the strong MnCO bending bands, which are located in the same region. The isotopic shift is of the same order as for Cp_2 Fe [15] and CTM [11]. As for in-plane CH bending modes, we have observed in the spectra of PTM three bands of ρ(CH) with the positions near the corresponding Cp-ring bands. The fourth band is apparently weak. Probably the weak 1047 cm^{-1} band corresponds to this mode.

For CTM the ρ(CH) A_1 and E_1 modes are observed at 837 and 845 cm^{-1} respectively. The previous assignment must be changed because the 837 cm^{-1} line is polarized in the solution Raman spectra.

2. *Skeletal modes*

The vibrations of the $LMn(CO)_3$ moiety, taking the ligand as a point mass, can be classified on the basis of C_{3v} symmetry. 18 normal modes are expected, divided between the symmetry classes as follows: $5A_1 + A_2 + 6E$, including 2 CO stretching modes ($A_1 + E$), 2 MnCO stretching modes ($A_1 + E$), 4 MnCO bending modes ($A_1 + A_2 + 2E$), 2 CMnC bending modes ($A_1 + E$), Mn—L stretching mode (A_1) and LMnC bending mode (E). A_1 and E modes are IR and Raman active, A_2

mode is forbidden in both types of spectra. Taking into consideration the actual structure of the molecule three additional modes are expected: Two ring tilts and torsional ligand vibration with respect to the $Mn(CO)_3$ group.

(a) CO stretching modes. Two CO stretching bands are found in the IR solution spectra of PTM near 1953 and 2038 cm^{-1} in accord with C_{3v} symmetry. The latter line is polarized in the Raman spectrum and therefore assigned to A_1mode. The A_1 line in the Raman spectrum has a lesser intensity than the ν(CO) (E) line. This anomaly was noted earlier for some carbonyl complexes [16,17] and explained by the different signs of the polarizability derivatives along the CO bond and perpendicular to it.

The ν(CO) frequencies for PTM are somewhat higher than those of CTM (1938 and 2025 respectively) and are similar to the frequencies of the CTM derivatives with the acceptor substituents in the ring [18]. Thus the replacement of the CH group by a nitrogen atom causes the same shift of the CO stretching bands as the introduction of the acceptor substituents in the ring.

(b) Metal—ring stretching modes. The strong polarized Raman line at 347 cm^{-1} for PTM is assigned to the symmetric M—L mode (353 $cm^{-1}$for CTM). The corresponding band in the IR spectrum was not observed. The ring tilts for Cp-derivatives are located as a rule in the same region, and have a frequency somewhat higher than the symmetric mode, more intense in the IR spectra and far weaker in the Raman spectra. Actually for CTM the IR band at 395 cm^{-1} was assigned to this mode. For PTM in the IR spectra of the solid, two medium intensity bands at 375 and 384 cm^{-1} have been found. The two corresponding depolarlized lines in the solution Raman spectra have been observed; the appearance of the doublet is connected with the lowering of the symmetry from C_{5v} for Cp-derivatives to C_s for pyrrolyl derivatives and with the splitting of the E_1 mode to A' and A''. The two additional metal—ring stretching modes for PTM (E_2 mode for Cp-derivatives) are the out-of-plane ring modes (see above).

(c) Metal—carbonyl stretching modes. The M—CO stretching modes are observed usually in metal carbonyl spectra between 400 and 550 cm^{-1}. In this region for PTM a strong polarized Raman line at 498 cm^{-1} was found and therefore assigned to ν(Mn—CO) (A_1). To the ν(Mn—CO) (E) mode the band 487 cm^{-1} is assigned. The corresponding CTM modes are located at 499 and 487 cm^{-1}.

*(d) Metal—carbonyl bending modes.*For CTM the strong IR bands 667, 637 and 542 cm^{-1} have been assigned to the modes E_1, E_2 and A_1 respectively [4]. Our study of the CTM Raman spectrum demonstrated that 667 cm^{-1} line is polarized and consequently must be assigned to the A_1 mode. Such assignment is in accordance with the data for benzenechromium tricarbonyl [6,7], where the frequencies are very similar to CTM (664, 632 and 541 cm^{-1}) and the 664 cm^{-1} line is also polarized in the Raman spectrum. The spectra of PTM almost correspond to the CTM spectra and the assignment is made by analogy. The 667 cm^{-1} IR band, which located in the same region, shifts to 590 cm^{-1} for PTM-d_4 and assigned therefore to the ring vibration (see above). The width of 633 and 535 cm^{-1} bands and the splitting of the last band into the doublet in the IR spectrum of the solid support the assignment of these bands to the degenerate vibrations.

(e) CMnC bending modes. Three bands of the skeletal bending vibrations below 200 cm^{-1} are expected. In the Raman spectra of PTM and CTM solutions

only the lines at 104 and 100 cm^{-1} respectively have been observed. The data are insufficient for symmetry assignment and the separation of the internal molecular vibrational bands from the lattice vibrations.

Note
When this report was prepared for publication the work with the new assignment of the vibrational spectra of CTM appeared [19]. The results coincide in general with ours.

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