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The Infrared Spectra and Normal Coordinate Treatments of L_3Sn-$Mn(CO)_5$ (L=Cl, Br, CH_3, and C_6H_5)

Satoru ONAKA[1)]

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo

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The infrared absorption spectra (2200—60 cm^{-1}) have been measured for four analogous compounds, Cl_3Sn–$Mn(CO)_5$, Br_3Sn–$Mn(CO)_5$, $(CH_3)_3Sn$–$Mn(CO)_5$, and Ph_3Sn–$Mn(CO)_5$. Normal coordinate analysis has been made for three molecules-Cl_3Sn–$Mn(CO)_5$, Br_3Sn–$Mn(CO)_5$, and $(CH_3)_3Sn$–$Mn(CO)_5$- on the basis of a modified Urey-Bradley force-field. The calculated frequencies attain close agreement with validly-assigned frequencies. The force constant, K(Sn–Mn), for each molecule varies with the substituent on the tin atom, and increases in the order of: K(Sn–Mn) of Cl_3Sn–$Mn(CO)_5$>K(Sn–Mn) of Br_3Sn–$Mn(CO)_5$>K(Sn–Mn) of $(CH_3)_3Sn$–$Mn(CO)_5$. The vibrational eigenvectors reveal that the Sn–Mn stretching vibrational modes are considerably coupled with other vibrational modes, especially with CMnC deformation and axial MnC stretching modes.

Recently, the nature of M–Co bonds (M=Si, Ge, and Sn) has been studied by means of NQR[2,3)] and the ^{119}Sn-Mössbauer effect,[4–6)] and it has been suggested that the stability of these compounds can be associated or correlated with M–Co π bonding.

The present author has also reported that the σ and π characteristics of the Sn–Mn bondings of a series of $R_{3-x}X_xSn$–$Mn(CO)_5$ compounds are extensively affected by the quantity of halogen on the tin atom; he reached this conclusion on the basis of ^{55}Mn- and ^{1}H-NMR and ^{119}Sn-Mössbauer-effect studies.[7,8)]

Although it is well recognized that the vibrational analysis is very profitable in determining the strengths of the bonds of interest as a total effect of σ and π interactions between atoms, especially in determining the strengths of the metal-metal bonds, such analysis has been successfully achieved in only a few cases[9–11)] because of the many difficulties which must be overcome. However, the diatomic or pseudo-diatomic models have been employed to obtain information about the strengths of the metal-metal bonds.[12,13)] According to Watters *et al.*,[10)] however, diatomic or pseudo-diatomic models may not be accurate for Cl_3-Si–$Co(CO)_4$ and Cl_3Ge–$Co(CO)_4$ because of the large extent of vibrational coupling with other modes.

The present author has now aimed to clarify the nature of the Sn–Mn bond further by making vibrational analyses of the series of L_3Sn–$Mn(CO)_5$ (L=Cl, Br and CH_3) compounds as a part of the study of the Sn–Mn bond. The present paper reports the infrared spectra of four molecules, Cl_3Sn–$Mn(CO)_5$, Br_3Sn–$Mn(CO)_5$, $(CH_3)_3Sn$–$Mn(CO)_5$, and Ph_3Sn–$Mn(CO)_5$, spectral assignments, their normal coordinate analyses, and the characterizations of the Sn–Mn bonds.

Experimental

The samples were prepared by the methods described in the literature.[14,15)] The purity of samples was determined by elemental analyses, by melting- or decomposing-point measurements, and by studying the infrared spectra (CO stretching region); the present values are in good agreement with previously published values.[15–17)]

The infrared spectra in the CO stretching region were measured with a Hitachi EPI-G2 spectrometer in a hexane solution with a KBr liquid cell. The Nujol mull samples were also examined with Hitachi EPI-G2, EPI-L spectrometers and a FIS-1 double-beam vacuum spectrophotometer in the region from 2200 to 60 cm^{-1}. The results are summarized in Table 1 and in Fig. 1.

Normal Coordinate Treatment

Spectral Assignment. The vibrational assignment for each molecule has been made by comparing the spectra of the four compounds with one another and by taking into consideration the calculated frequencies. The reported assignments of analogous compounds were also taken into account.[12,15–22)]

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TABLE 1. OBSERVED INFRARED SPECTRA, VIBRATIONAL ASSIGNMENTS AND CALCULATED FREQUENCIES

Observed frequencies cm^{-1}	Intensity	Calculated frequencies cm^{-1}	Assignment	Approximate vibrational modes
Cl_3Sn-$Mn(CO)_5$				
2126	m	2125	S_5	CO str.
2046	vs	2048	S_{19}	CO str.
2040	s	2041	S_4	CO str.
650	vs	649	S_{13}	MnCO def.
642	vs	639	S_{27}	MnCO def.
~570	sh, vw	567	S_{28}	MnCO def.
548	vw			
535	vw	539	S_{16}	MnCO def.
497	vw			
451	s	447	S_{18}	MnC str.
406	w	407	S_1	MnC str.
394	vw	395	S_2	MnC str.
345	vs, br	$\begin{cases}354\\334\end{cases}$	$\left.\begin{matrix}S_{20}\\S_7\end{matrix}\right\}$	SnCl str.
240	w			
197	s	197	S_8	Sn-Mn str.
130	s	$\begin{cases}128\\125\end{cases}$	S_{21} S_{23}	ClSnCl def. CMnC def.
112	vs	$\begin{cases}120\\111\end{cases}$	$\left.\begin{matrix}S_9\\S_{24}\end{matrix}\right\}$	ClSnCl def. CMnC def.
85	w	82	S_9	ClSnCl def.
65	s	78	S_{25}	CMnSn def.
Br_3Sn-$Mn(CO)_5$				
2124	m	2124	S_5	CO str.
2045	vs	2047	S_{19}	CO str.
2038	s	2038	S_4	CO str.
645	vs	648	S_{13}	MnCO def.
630	vs	635	$S_{27}+S_{26}$	MnCO def.
~565	vw	563	$S_{27}+S_{28}$	MnCO def.
534	vw	539	S_{16}	MnCO def.
495	vw			
448	s	447	S_{18}	MnC str.
406	vw	404	S_1	MnC str.
392	w	395	S_2	MnC str.
240	vs	$\begin{cases}244\\216\end{cases}$	$\left.\begin{matrix}S_{20}\\S_7\end{matrix}\right\}$	SnBr str.
178	m	178	S_8	Sn-Mn str.
125	m	125	S_{23}	CMnC def.
108	m	$\begin{cases}112\\106\end{cases}$	S_{24} S_{10}	CMnC def. CMnC, CMnSn-def.
90	s	85	S_{21}	BrSnBr def.
75	s , br	69	S_{21}	BrSnBr def.
		61	S_9	BrSnBr def.
$(CH_3)_3Sn$-$Mn(CO)_5$[a]				
2091	m	2091	S_5	CO str.
2027	w	2029	S_6	CO str.
2001	s	2001	S_4	CO str.
1995	vs	1996	S_{19}	CO str.
662	vs	663	S_{13}	MnCO def.
650	vs	654	S_{27}	MnCO def.
583	vw	578	$S_{27}+S_{28}$	MnCO def.
~555	vw, sh			
545	w	539	S_{16}	MnCO def.
518	s	514	S_{20}	Sn-CH_3 str.
502	s	503	S_7	Sn-CH_3 str.
482	s	481	S_{18}	MnC str.
~425	w, sh	420	S_2	MnC str.
413	m	413	S_1	MnC str.
179	s	179	S_8	Sn-Mn str.
164	m	163	S_{21}	CSnC def.
130	m	$\begin{cases}133\\125\end{cases}$	S_9 S_{25}	CSnC def. CMnC, CMnSn def.
108	m	113	S_{24}	CMnC, CMnSn def.
90	m	$\begin{cases}91\\82\end{cases}$	S_{10} S_{22}	CMnC, CMnSn def. MnSnC def.
Ph_3Sn-$Mn(CO)_5$[b]				
2095	m		S_5	CO str.
2029	w		S_6	CO str.
2004	vs		$\begin{cases}S_4\\S_{20}\end{cases}$	CO str. CO str.
657	vs		S_{13}	MnCO def.
642	vs		S_{27}	MnCO def.
615	vw			
~590	vw, sh			
557	w			
545	w			
481	s		S_{18}	MnC str.
450	s		Absorption due to a mono-substituted C_6H_5 ring.	
428	vw			
420	vw			
413	w			
394	vw			
256	vs			
240	vs			
208	s			
204	s			
170	m		S_8	Sn-Mn str.
151	w			
120	w			
95	w			
85	w			

a) Absorptions due to a CH_3 group on tin atom which are observed at NaCl region are excluded from the Table.

b) Absorptions due to a C_6H_5 group on tin atom which are observed at NaCl region are excluded from the Table.

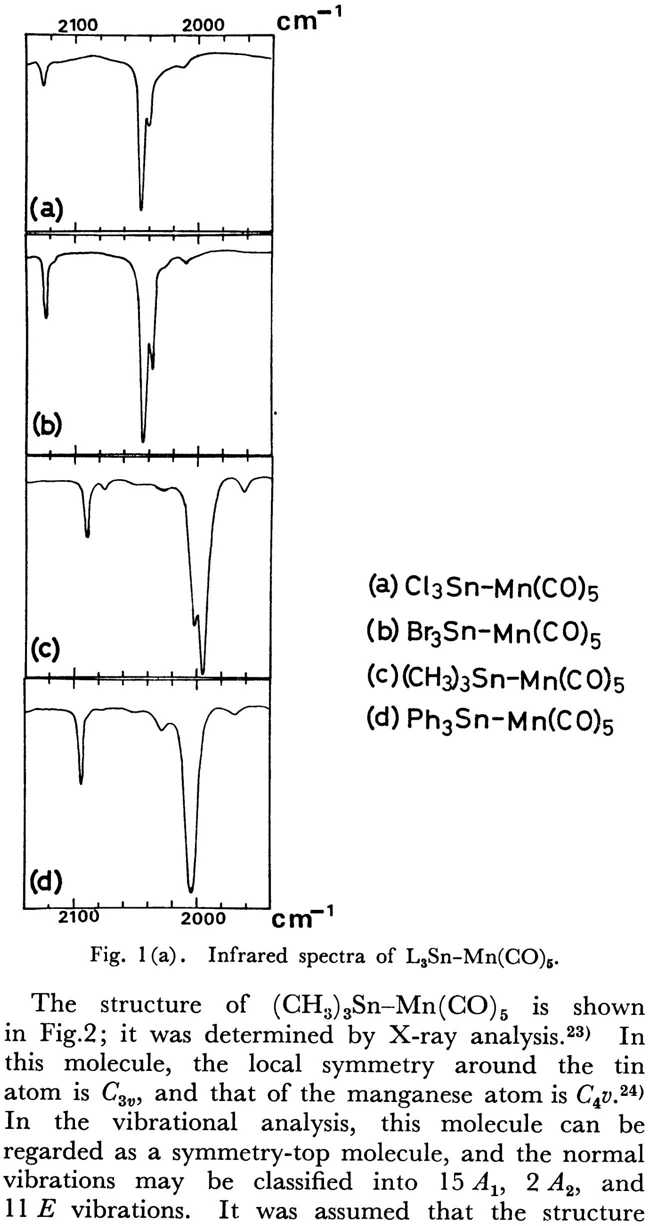

Fig. 1(a). Infrared spectra of L_3Sn-$Mn(CO)_5$.

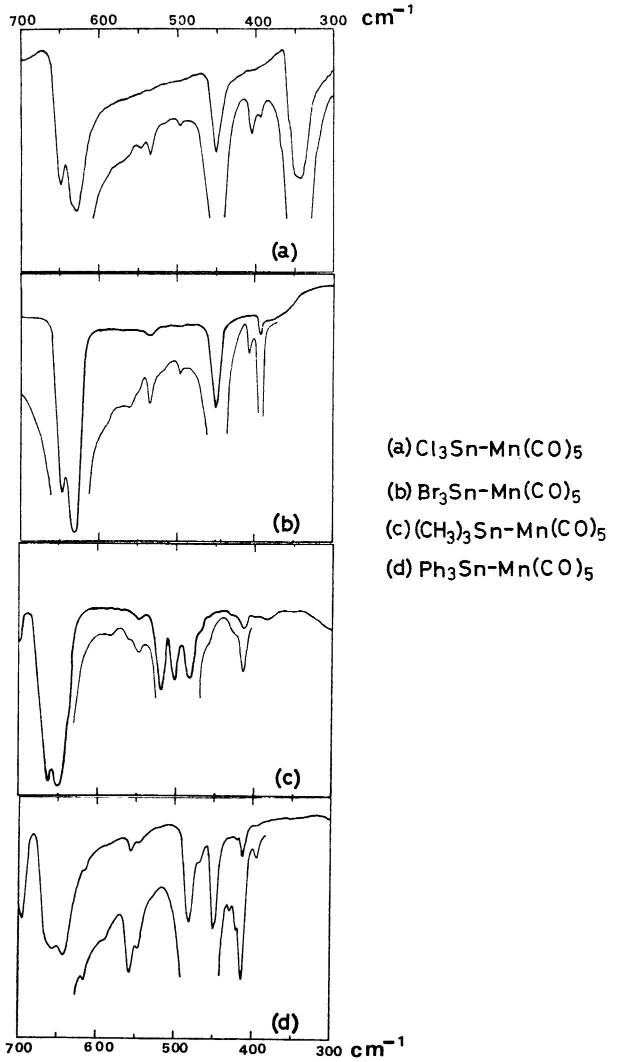

Fig. 1(b). Infrared spectra of L_3Sn-$Mn(CO)_5$.

The structure of $(CH_3)_3Sn$–$Mn(CO)_5$ is shown in Fig.2; it was determined by X-ray analysis.[23] In this molecule, the local symmetry around the tin atom is C_{3v}, and that of the manganese atom is $C_{4}v$.[24] In the vibrational analysis, this molecule can be regarded as a symmetry-top molecule, and the normal vibrations may be classified into 15 A_1, 2 A_2, and 11 E vibrations. It was assumed that the structure of X_3Sn–$Mn(CO)_5$ was the same as that of $(CH_3)_3Sn$–$Mn(CO)_5$. The close resemblance of their vibrational spectra supports this assumption.

The outline of the vibrational assignments is shown below.

The 2200—1900 cm⁻¹ Region (*CO Stretching Region*): According to many reports on L–$Mn(CO)_5$-type compounds,[13,25–33] the highest-frequency absorption with a medium-to-weak intensity is assigned to the A_1 vibration; the most intense absorption is assigned to the E vibration due to the equatorial CO stretching mode, and the absorption with a medium-to-strong intensity to the A_1 vibration due to the axial CO stretching mode.

The 700—500 cm⁻¹ Region: The highest-frequency absorption with a strong intensity is assigned to the A_1 vibration due to the equatorial MnCO bending mode, and the most intense absorption in this region is tentatively assigned to the E vibration due to the axial MnCO bending mode. The strong absorptions at 518 and 502 cm⁻¹ for $(CH_3)_3Sn$–$Mn(CO)_5$ are assigned to the Sn–CH_3 stretching vibrations.[20]

The 500—350 cm⁻¹ Region: The highest-frequency absorption with the strongest intensity in this region is assigned to the E vibration, and the weak absorptions around 400 cm⁻¹ are assigned to the A_1 vibrations of the MnC stretching modes. The strong absorption at 450 cm⁻¹ for Ph_3Sn–$Mn(CO)_5$ arises from the vibration of a mono-substituted benzene ring.[19]

The 350—200 cm⁻¹ Region: The assignments of

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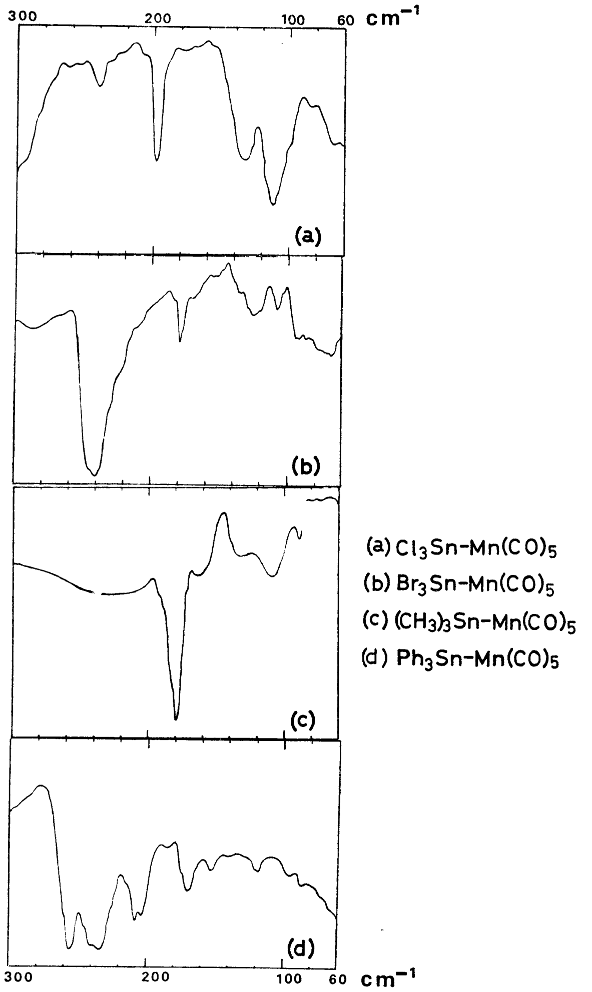

Fig. 1(c). Far-infrared spectra of $L_3Sn-Mn(CO)_5$.

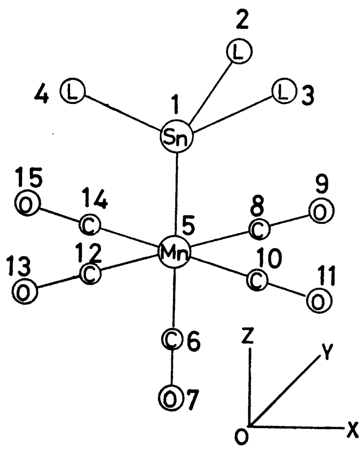

Fig. 2(a). The structure of $L_3Sn-Mn(CO)_5$.

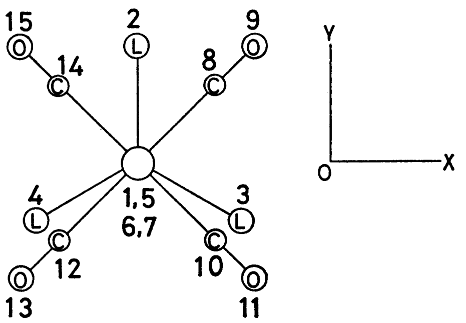

Fig. 2(b). The structure of $L_3Sn-Mn(CO)_5$.

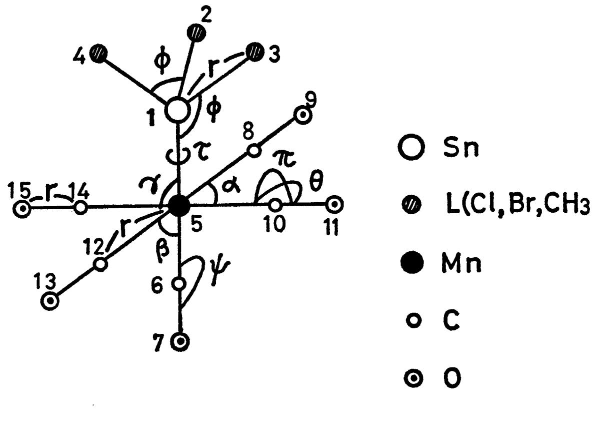

Fig. 3. Internal coordinates of $L_3Sn-Mn(CO)_5$.

the Sn–L stretching vibrations for each molecule are made on the basis of the assignments reported for SnX_4,[21] $Sn(CH_3)_3X$,[20] $SnPh_4$, and $SnPh_3X$.[19] The very strong and broad band at 345 cm^{-1} for $Cl_3Sn-Mn(CO)_5$ is assigned to the SnCl stretching vibration, and the similar band at 240 cm^{-1} for $Br_3Sn-Mn(CO)_5$, to the SnBr stretching vibrations.

The 200—170 cm^{-1} Region: The bands with strong to medium intensities observed at 197, 178, 179, and 170 cm^{-1} for $Cl_3Sn-Mn(CO)_5$, $Br_3Sn-Mn(CO)_5$, $(CH_3)_3Sn-Mn(CO)_5$, and $Ph_3Sn-Mn(CO)_5$ respectively are assigned to the Sn–Mn stretching vibrations.

The 170—60 cm^{-1} Region: For $Cl_3Sn-Mn(CO)_5$, the strong bands at 130 and 112 cm^{-1} are observed.

These bands may be assigned to the deformation-vibrations of the $SnCl_3$ group. The bands observed at 125 and 108 cm^{-1} for $Br_3Sn-Mn(CO)_5$ may be assigned to the skeletal CMnC bending modes of the *E* species. The manganese carbonyl, $Mn_2(CO)_{10}$, also has two strong absorptions, at 120 and 110 cm^{-1}, which are due to the CMnC bending modes. The strong bands at 90—70 cm^{-1} for this molecule may be assigned to the $SnBr_3$ deformation-vibrations.[21] The bands at 160 and 130 cm^{-1} with medium intensities for $(CH_3)_3Sn-Mn(CO)_5$ may be assigned to the CSnC deformation-vibrations. The absorption at 110 cm^{-1} for the $(CH_3)_3Sn-Mn(CO)_5$ molecule may be assigned to the CMnC skeletal bending mode of the *E* species.

All the vibrational assignments are listed in Table 1.

The Procedure of Calculation. Frequency calculations were made for $Cl_3Sn-Mn(CO)_5$, $Br_3Sn-Mn(CO)_5$, and $(CH_3)_3Sn-Mn(CO)_5$ molecules on the basis of Wilson's GF matrix method,[34] in which CH_3 group was treated as one unit. The symmetry coordinates are constructed based on the C_{3v} symmetry group and C_{4v} for $Mn(CO)_5$ group respectively, which are listed

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[34] E. B. Wilson, *J. Chem. Phys.*, **9**, 76 (1941).

Table 2. Symmetry coordinates used in the calculation

Symmetry Species	Vibrational Modes	Symmetrys Coordinates*
A_1	MnC stretching	$S_1=\Delta r_1$
		$S_2=\Delta(r_2+r_3+r_4+r_5)$
		$S_3=\Delta(r_2-r_3+r_4-r_5)$
	CO stretching	$S_4=\Delta r_6$
		$S_5=\Delta(r_7+r_8+r_9+r_{10})$
		$S_6=\Delta(r_7-r_8+r_9-r_{10})$
	SnL stretching	$S_7=\Delta(r_{11}+r_{12}+r_{13})$
	SnMn stretching	$S_8=\Delta r_{14}$
	LSnL deformation	$S_9=\Delta(\phi_1+\phi_2+\phi_3-\phi_4-\phi_5-\phi_6)$
	CMnC, CMnSn deformation	$S_{10}=\Delta(\beta_1+\beta_2+\beta_3+\beta_4-\gamma_1-\gamma_2-\gamma_3-\gamma_4)$
		$S_{11}=\Delta(\beta_1-\beta_2+\beta_3-\beta_4-\gamma_1+\gamma_2-\gamma_3+\gamma_4)$
	CMnC deformation	$S_{12}=\Delta(\alpha_1-\alpha_2+\alpha_3-\alpha_4)$
	MnCO deformation	$S_{13}=\Delta(\pi_1+\pi_2+\pi_3+\pi_4)$
		$S_{14}=\Delta(\pi_1-\pi_2+\pi_3-\pi_4)$
		$S_{15}=\Delta(\theta_1-\theta_2+\theta_3-\theta_4)$
A_2	MnCO deformation	$S_{16}=\Delta(\theta_1+\theta_2+\theta_3+\theta_4)$
	Torsion	$S_{17}=\Delta\tau$
E	MnC stretching	$S_{18}=\Delta(r_2+r_3-r_4-r_5),\ \Delta(r_2-r_3-r_4+r_5)$
	CO stretching	$S_{19}=\Delta(r_7+r_8-r_9-r_{10}),\ \Delta(r_7-r_8-r_9+r_{10})$
	SnL stretching	$S_{20}=\Delta(r_{12}-r_{13}),\ \Delta(2r_{11}-r_{12}-r_{13})$
	LSnL deformation	$S_{21}=\Delta(\phi_2-\phi_3),\ (2\phi_1-\phi_2-\phi_3)$
	LSnMn deformation	$S_{22}=\Delta(\phi_5-\phi_6),\ \Delta(2\phi_4-\phi_5-\phi_6)$
	CMnC deformation	$S_{23}=\Delta(\alpha_1-\alpha_3),\ \Delta(\alpha_2-\alpha_4)$
	CMnC, CMnSn deformation	$S_{24}=\Delta(\beta_1+\beta_2-\beta_3-\beta_4-\gamma_1-\gamma_2+\gamma_3+\gamma_4),$
		$\Delta(\beta_1-\beta_2-\beta_3+\beta_4-\gamma_1+\gamma_2+\gamma_3-\gamma_4)$
	CMnC, CMnSn deformation	$S_{25}=\Delta(\beta_1+\beta_2-\beta_3-\beta_4+\gamma_1+\gamma_2-\gamma_3-\gamma_4),$
		$\Delta(-\beta_1+\beta_2+\beta_3-\beta_4-\gamma_1+\gamma_2+\gamma_3-\gamma_4)$
	MnCO deformation	$S_{26}=\Delta(\theta_1-\theta_2-\theta_3+\theta_4),\ \Delta(\theta_1+\theta_2-\theta_3-\theta_4)$
	MnCO deformation	$S_{27}=\Delta\psi_1,\ \Delta\psi_2$
	MnCO deformation	$S_{28}=\Delta(-\pi_1-\pi_2+\pi_3+\pi_4),\ \Delta(\pi_1-\pi_2-\pi_3+\pi_4)$

r_1—r_5 : Mn-C bonds
r_6—r_{10} : C-O bonds
r_{11}—r_{13} : Sn-L bonds
r_{14} : Sn-Mn bond
ϕ_1—ϕ_3 : L-Sn-L angles
ϕ_4—ϕ_6 : L-Sn-Mn angles
α_1—α_4 : C-Mn-C angles (in-plane)
β_1—β_4 : C-Mn-C angles
γ_1—γ_4 : C-Mn-Sn angles
π_1—π_4 : Mn-C-O angles (out-of-plane)
θ_1—θ_4 : Mn-C-O angles (in-plane)
ψ_1—ψ_2 : Mn-C-O angles (trans to Sn)
τ : Torsional angle around the Sn-Mn bond
* : Normalization constants are excluded.

in Table 2. The internal coordinates used are shown in Fig. 3. A normal coordinate analysis is made by solving a secular equation of 39th order. The values of the bond lengths, r(Sn–Mn), r(Mn–C), and r(C–O), listed in Table 3 are taken from the average values of $(CH_3)_3Sn-Mn(CO)_5$ and $Ph_3Sn-Mn(CO)_5$.[23,24] The bond lengths, r(Sn–Cl) and r(Sn–Br), are taken from the $(CH_3)SnCl_3$, and $(CH_3)SnBr_3$ values,[35] which were determined by electron-diffraction measurements. The L–Sn–L and L–Sn–Mn angles are assumed to be tetrahedral angles, and the C–Mn–C and Sn–Mn–C angles are assumed to be 90° on the basis of the crystal data.[23,24]

Table 3. The geometrical parameters used in calculation

r(Mn-C) = 1.78_2Å[a]	∠L-Sn-L = tetrahedral angle[a]
r(C-O) = 1.16_6Å[a]	∠L-Sn-Mn = tetrahedral angle[a]
r(Sn-Mn) = 2.67_4Å[a]	∠C-Mn-C = 90°[a]
r(Sn-CH$_3$) = 2.13Å[a]	
r(Sn-Cl) = 2.32Å[b]	
r(Sn-Br) = 2.45Å[b]	

a) cited from the literature[23,24]
b) cited from the literature[35]

The modified Urey-Bradley force field is used for the calculation,[36] and twenty-four force constants are used for each molecule. The values of them are given in Table 4. The K, H, F, Y, and P symbols represent the stretching, deformation, repulsion, torsion and stretch-stretch interaction force constants respectively. The suffixes, a, e, i, o, t, and c, are explained in Table 4. The initial values of K_a(CO), K_e(CO), P_t(CO, CO), and P_c(CO, CO) of the $Mn(CO)_5$ moiety are obtained by the Cotton-Kraihanzel method.[26] The other force constants for the $Mn(CO)_5$ part are taken from the values for $Mo(CO)_6$

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36) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).

TABLE 4. FORCE CONSTANTS IN md/Å

	Cl_3Sn-Mn-$(CO)_5$	Br_3Sn-Mn-$(CO)_5$	$(CH_3)_3Sn$-Mn-$(CO)_5$
K_a(MnC)	1.8	1.8	1.9
K_e(MnC)	2.2	2.2	2.5_7
K_a(CO)	16.9	16.8_5	16.2_6
K_e(CO)	17.2_3	17.2_0	16.3_0
K(SnMn)	1.0	0.82	0.7
K(SnL)	1.8	1.3_9	1.9_5
H(LSnL)	0.06	0.04	0.05_5
H(MnSnL)	0.02	0.02	0.01
H_e(CMnC)	0.15	0.15	0.15
H_a(CMnC)	0.15	0.15	0.15
H(CMnSn)	0.10	0.10	0.10
H_i(MnCO)	0.8	0.8	0.8
H_o(MnCO)	0.85	0.85	0.9
H_a(MnCO)	0.86	0.83	0.9
F(L···L)	0.12	0.12	0.07
F(Mn···L)	0.05	0.05	0.05
F_a(C···C)	0.01	0.01	0.01
F_e(C···C)	0.01	0.01	0.01
F(C···Sn)	0.01	0.01	0.01
Y(Mn-Sn)[a)]	0.005	0.005	0.005
P(MC, CO)	0.5	0.5	0.4
P(MC, MC)	0.4	0.4	0.4
P_t(CO, CO)	0.3	0.3	0.36
P_c(CO, CO)	0.17	0.17	0.22

a) md·Å
a : axial CO group
e) equatorial CO groups
i and *o* : in-plane and out-of plane MnCO bending modes of the square planar $Mn(CO)_4$ part.
t : *trans*
c : cis

calculated by Jones.[37)] The initial set of force constants of the SnL_3 groups are taken from the SnL_3X and the SnL_4 molecules.[20,21)] The initial values of K(SnMn) are estimated on the basis of the diatomic models from the IR frequencies. The values of the repulsion force constants, F(Mn···L) and F(C···Sn), are estimated from the Lennard-Jones potentials for inert gasses.[38–40)] The initial value of H(MnSnL) is estimated considering the H(CMnC) and H(LSnL) values. The value of Y(Mn–Sn) is arbitrarily assumed to be 0.005 md·Å, taking into account the values of the ethane derivatives.[41)]

The numerical calculation was carried out by using a HITAC 5020*E* of the Computation Center of the University of Tokyo and programs set up in the laboratory of Professor T. Shimanouchi.[42)] First, the force constants of Br_3Sn–$Mn(CO)_5$ were determined. The values of the force constants were adjusted to get the best fit of the calculated frequencies with the observed ones, with reference made to the Jacobian matrix elements. Then, the frequencies of the other two molecules were calculated using the same values of the force constants as those of Br_3Sn–$Mn(CO)_5$, except those which had to be changed essentially.

Results

The final set of all the force constants are listed in Table 4. The frequencies calculated by means of these force constants are in good agreement with the observed values, as is shown in Table 1.

The eigenvectors here obtained show that the vibrational modes associated with the Sn–Mn stretching vibration are extensively coupled with the other vibrational modes, especially with the CMnC deformation and axial MnC stretching modes. The vibrational coupling in the ν(Sn–Mn) with other vibrations for Br_3Sn–$Mn(CO)_5$ is different from those of the other two molecules, and the SnBr stretching vibration is appreciably mixed. The purities of the vibrational modes assigned to the Sn–Mn stretching vibrations are evaluated from the potential energy distribution to the Sn–Mn stretching coordinate (PED), shown in Table 5.

TABLE 5. POTENTIAL ENERGY DISTRIBUTION MATRIX IN Sn–Mn STRETCHING VIBRATION

Approximate vibrational modes		$(PED)_{ij}$		
		Cl_3Sn-$Mn(CO)_5$	Br_3Sn-$Mn(CO)_5$	$(CH_3)_3Sn$-$Mn(CO)_5$
S_1	Mn-C str.	11	8	8
S_7	Sn-L str.		16	
S_8	Sn-Mn str.	68	46	64
S_9	L-Sn-L def.	5		6
S_{10}	C-Mn-C def.	14	22	24
S_{13}	Mn-C-O def.	4	5	5

$$(PED)_{ij}=\frac{(L_{ij})^2\cdot(F_s)_{ii}}{\lambda_j}\times 100$$

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42) Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo.

Discussion

For metal carbonyl compounds, it is well known that two types of electron donations act between the metal, M, and the ligand, CO, namely σ-electron donation from CO to M and π-electron back-donation from M to CO, and that the variation in the π-interaction between L and M in $LM(CO)_n$-type metal carbonyl compounds strongly affects the force constants, K(CO) and K(MC), in the following manner. The ligand, L, and the CO can both undergo π-bonding with the metal d orbitals. This π-interaction involves the back-donation of metal *d* orbitals to the vacant antibonding CO orbitals. If the ligand, L, can also accept metal d_π electrons into suitable π-type orbitals, it will compete with the CO for *d* electrons of the transition metal. The π-acceptor capability of L will also influence the force constants, K(CO) and K(MC). The grater the π-bonding to L, the less the electron density which will enter the antibonding orbitals of the CO, and the greater the CO stretching force constant, and the smaller the MC stretching force constant.[43-45]

The values of the force constants listed in Table 4 show that the strength of the Sn–Mn bond is strongly affected by the electronegativity of the L on the L_3Sn group; moreover, the smaller the values of K(MnC), the larger the values of K(CO) and K(SnMn) become. These facts suggest that not only the σ-electron donation but also the π-electron back-donation act on the Sn–Mn bond, and that the strength of the π-bond nature between Sn and Mn also varies with the substituent on the Sn atom. Therefore, it can be deduced that the π-bond strengths of the Sn–Mn bond increase in the order: $(CH_3)_3Sn{-}Mn(CO)_5 < Br_3Sn{-}Mn(CO)_5 < Cl_3Sn{-}Mn(CO)_5$, according to the above considerations and the force constants listed in Table 4. The difference in the π-bond strength between chloro- and bromo-complexes is, however, considered not to be large, because the K(MnC) and K(CO) force constants, which are a measure of the π-interaction between Sn and Mn, of the two compounds closely resemble each other. The values of the K(SnMn) force constants, which are a direct measure of the total bond strength, $(\sigma+\pi)$, between Sn and Mn, are in the same order, but the difference in the K(SnMn) values of the two halogen complexes is much more enhanced.[46] One possible origin of this enhancement is due to the assumption of the same Sn–Mn bond length for these two compounds.

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[43] A "spectrochemical series" for π bonding of ligands L (L= NO, PR_3, AsR_3, SbR_3, phen, dien and so on) have been obtained by making use of the IR data (ν(CO)): M. Bigorgne, *J. Organometal. Chem.*, **1**, 101 (1963); F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962), and *Inorg. Chem.*, **2**, 533 (1963); F. A. Cotton, *ibid.*, **3**, 702 (1964); G. R. Dobson, *ibid.*, **4**, 1673 (1965); W. D. Horrcks and R. C. Taylor, *ibid.*, **2**, 723 (1963).

[44] W. A. G. Graham, *ibid.*, **7**, 315 (1968).

[45] L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radio-Chem.*, **11**, 53 (1969).

[46] On the basis of ^{55}Mn–NMR data, the electronic nature around the Mn nucleus in the $Br_3Sn{-}Mn(CO)_5$ is in close resemblance to that of $Cl_3Sn{-}Mn(CO)_5$.