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The Crystal Structure of Trichloroti-npentacarbonylmanganese, Cl_3Sn–$Mn(CO)_5$

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The crystal structure of trichlorotin–pentacarbonylmanganese, Cl_3Sn–$Mn(CO)_5$, has been determined by means of X-ray diffraction. The crystal is monoclinic; $a=14.10(1)$, $b=13.38(5)$, $c=13.27(2)$ Å, and $\beta=97.39(21)°$ with the $P2_1/c$ space group and with $Z=8$. The structure, established by the heavy-atom method, has been refined by a least-squares method based on 2581 reflections collected by diffractometry to give an R value of 10%. The asymmetric unit contains two quite similar molecules. The geometry around the tin atom is distorted tetrahedrally, while the manganese atom exhibits a distorted octahedral coordination. The four equatorial carbonyl groups are displaced from the equatorial plane toward the tin atom. There is an approximate mirror plane through the Sn–Mn–CO(axial) axis. The Sn–Mn bond distance, 2.590(5) Å, is shorter by about 0.08 Å than that of the triphenyl and trimethyl analogues. The mean Mn–C distance of 1.87 Å is longer than that of the trimethyl analogue. These changes in bond distances may be interpreted in terms of the π-interaction between the two metal atoms, which is more pronounced in the chloro-derivative than in the methyl derivative.

In a series of papers concerning the X_3M–Mn-$(CO)_{5-n}L_n$ compounds (X stands for CH_3, C_6H_5, Cl, Br, and I; M for Si, Ge, and Sn; L for $P(C_6H_5)_3$, $As(C_6H_5)_3$, and $Sb(C_6H_5)_3$, and $n=0$ or 1), the effect of IV b metal atoms or the effect of the substituents of the component-metal atoms on the nature of the strength of the M–Mn bonds has been studied by means of IR,[1–4] NMR,[5] NQR,[6] and the ^{119}Sn-Mössbauer effect.[7,8] It has been concluded that the π-interaction between manganese and IV b metal atoms is influenced by the substituent, X or L. In order to provide further evidence of the effect of the substituents on the M–Mn bond nature and in order to confirm other results or estimations previously obtained,[4,6] it is desirable to obtain information regarding the details of the molecular structure in this series of compounds by the X-ray diffraction method. However, no trihalogeno compound, X_3Sn–$Mn(CO)_5$, has yet been subjected to X-ray crystal structure analysis,[9] though the crystal structures of $(C_6H_5)_3Sn$–$Mn(CO)_5$,[10] $(CH_3)_3Sn$–Mn-$(CO)_5$,[11] and $(C_6H_5)_3Sn$–$Mn(CO)_4P(C_6H_5)_3$[12] have been determined by Bryan *et al.* This may be partly because of the instability of these trihalogeno compounds toward X-rays.[13] We succeeded in the preparation of stable and suitable crystals of Cl_3Sn–$Mn(CO)_5$ for X-ray analysis from a dichloromethane solution. In this paper, we wish to report on the crystal structure of Cl_3Sn–$Mn(CO)_5$ and to discuss the effect of the Cl atom as a substituent on the molecular geometry.

Table 1. Crystal data of Cl_3Sn–$Mn(CO)_5$

Chemical formula	$C_5O_5Cl_3MnSn$
Crystal system	monoclinic
Space group	$P2_1/c$
Cell dimensions; a	14.10 ± 0.01Å
b	13.38 ± 0.05
c	13.27 ± 0.02
β	$97.39\pm0.21°$
V	2483Å^3
Z	8
D_x	$2.25\ g\cdot cm^{-3}$
D_m	$2.30\ g\cdot cm^{-3}$

Experimental

Trichlorotin–pentacarbonylmanganese was synthesized by the method of Gorsich,[14] and the crystals of this compound were grown from various solutions in a form of pale yellow needles. Suitable crystals for X-ray analysis were obtained from crops from a dichloromethane solution.

Single-crystal X-ray Data. The space group and the lattice constants were determined from Weissenberg photographs; the latter were then refined by the least-squares method. The crystal data are given in Table 1. The intensity measurements were made by using two crystals, with dimensions of 0.29×0.35×0.37 mm and 0.29×0.35×0.41 mm, on a Rigaku four-circle automatic diffractometer. Mo $K\alpha_1$ radiation ($\lambda=0.7107$ Å) monochromated by graphite was used with a scintillation counter, an ω-2θ scan technique being employed. The scan speed was 4°/min in 2θ. Background measurements were made on both sides of every peak. 3585 reciprocal lattice points were surveyed in the $2\theta<45°$ range; a significant intensity was observed at 2581 points. Three standard reflections were measured every 50 measurements. The intensities for the second crystal were adjusted to those of the first crystal based on the three standard reflections. The intensities were corrected for the Lorents and polarization effects. No corrections were applied for absorption and extinction.

Determination of the Structure. All the calculations were carried out on a FACOM 230-60 computer at the Computation Center of Nagoya University, using the RSSFR-5 and HBLS-IV programs, which are included in the UNICS program system.[15] The positions of the tin atoms were deduced from the three-dimensional sharpened Patterson maps. The Fourier synthesis based on the positions of the tin atoms easily located the manganese atoms. The positions of the other atoms were readily determined from successive three-dimensional Fourier syntheses. A refinement of the structure was carried out by the block-diagonal least-squares method for thirty atoms in the asymmetric unit with isotropic thermal parameters. The unit weight was given for each reflection. The discrepancy index, R, was 11.7%. The difference Fourier synthesis at this stage left no appreciable peaks. A further refinement by the use of anisotropic thermal parameters reduced the R value to 9.98%. At the final stage, several strong reflections were excluded from the least-squares refinement, since they were considered to be

TABLE 3. FINAL POSITIONAL AND THERMAL PARAMETERS OF Cl_3Sn-$Mn(CO)_5$ WITH THEIR ESTIMATED STANDARD DEVIATIONS (in parantheses).

All values have been multiplied by 10^4. The anisotropic thermal parameters are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Molecule 1.									
Sn	9034(1)	1297(2)	1530(2)	40(1)	42(1)	42(1)	−3(2)	10(2)	10(2)
Mn	8928(3)	3112(4)	880(3)	31(3)	38(3)	35(3)	2(5)	9(4)	21(5)
Cl(1)	8011(7)	908(8)	2759(7)	70(6)	92(8)	64(7)	−41(12)	68(11)	−4(12)
Cl(2)	10474(7)	731(8)	2343(9)	56(6)	79(8)	93(8)	20(11)	−11(11)	26(14)
Cl(3)	8666(8)	−17(8)	359(9)	81(7)	64(7)	78(8)	−43(12)	5(12)	−54(12)
C(1)	8852(22)	4406(32)	442(23)	30(18)	117(35)	32(20)	21(41)	−5(31)	−38(45)
C(2)	10137(27)	3340(35)	1607(29)	60(24)	122(39)	69(29)	37(50)	102(45)	58(55)
C(3)	8318(30)	3496(21)	2080(24)	126(33)	12(18)	39(21)	1(37)	−132(45)	4(32)
C(4)	7760(19)	2859(38)	200(22)	7(14)	215(54)	15(17)	83(46)	−30(26)	2(49)
C(5)	9497(20)	2651(26)	−258(26)	26(16)	61(24)	74(26)	−8(33)	63(35)	70(43)
O(1)	8883(17)	5233(14)	133(18)	83(17)	9(11)	74(17)	48(23)	−8(28)	12(24)
O(2)	10839(18)	3437(21)	2074(22)	59(17)	84(22)	109(25)	−63(31)	−40(33)	18(38)
O(3)	7991(17)	3644(19)	2742(15)	85(17)	77(18)	24(13)	28(30)	72(24)	−11(26)
O(4)	7024(18)	2605(21)	−185(22)	69(18)	76(21)	98(23)	2(31)	17(33)	20(37)
O(5)	9828(19)	2417(17)	−949(18)	106(20)	38(15)	66(18)	13(29)	91(32)	10(27)
Molecule 2.									
Sn′	4016(1)	1296(2)	3219(2)	42(1)	42(1)	40(1)	−2(2)	23(2)	−4(2)
Mn′	3918(3)	3141(4)	3819(3)	31(3)	41(3)	35(3)	0(5)	16(4)	1(5)
Cl(1′)	5512(6)	704(8)	2919(8)	47(5)	66(7)	100(8)	33(10)	42(11)	−11(13)
Cl(2′)	3098(7)	874(7)	1673(7)	81(7)	66(7)	46(6)	−38(11)	−15(10)	−11(10)
Cl(3′)	3542(8)	43(8)	4303(8)	103(8)	68(7)	62(7)	−26(13)	61(12)	28(11)
C(1′)	3862(21)	4494(26)	4273(8)	36(18)	69(26)	51(22)	45(35)	64(34)	5(39)
C(2′)	3284(19)	3466(22)	2555(24)	20(16)	37(20)	59(22)	7(27)	−53(31)	11(34)
C(3′)	5109(20)	3355(19)	3367(22)	35(16)	12(15)	47(20)	4(25)	−7(30)	60(29)
C(4′)	4522(25)	2715(24)	5049(21)	86(25)	39(21)	19(18)	−44(38)	−22(35)	37(31)
C(5′)	2735(21)	2762(23)	4224(24)	34(17)	38(20)	58(23)	−62(31)	−22(32)	−46(35)
O(1′)	3860(21)	5263(20)	4572(21)	115(24)	73(20)	86(22)	99(36)	106(38)	−32(35)
O(2′)	2983(21)	3670(24)	1736(19)	107(23)	109(25)	51(17)	26(41)	39(32)	7(37)
O(3′)	5833(14)	3500(19)	3058(18)	32(12)	87(20)	71(18)	2(25)	20(24)	29(31)
O(4′)	4927(19)	2428(28)	5822(19)	72(18)	160(32)	56(18)	37(41)	36(30)	13(42)
O(5′)	2072(15)	2552(19)	4491(20)	34(13)	65(18)	104(22)	−27(25)	−1(27)	20(34)

seriously affected by the extinction effect. The neutral atomic scattering factors used were those listed in International Tables.[16] Table 2* lists the observed and calculated structure factors.

Results and Discussion

Table 3 gives the final positional and thermal parameters of atoms, along with their standard deviations. The molecular structure is shown in Fig. 1, along with the numbering scheme. The intramolecular atomic distances and bond angles are presented in Table 4. A projection of the molecule 1 down the Sn–Mn axis is drawn in Fig. 2. In Table 5, the torsional angles are listed. The molecular geometry of this compound is quite similar to those observed for triphenyltin-pentacarbonylmanganese and trimethyltin-pentacarbonylmanganese.[10,11] The geometry around the tin atom is distorted tetrahedrally, while that of the manganese atom is approximately octahedral.

As is shown in Table 4, the covalent Sn–Mn bond distances in Cl_3Sn–$Mn(CO)_5$ are 2.575(5) Å and 2.604(5) Å (average 2.59 Å), which are considerably shorter than those of $(CH_3)_3Sn$–$Mn(CO)_5$ (2.674 Å)

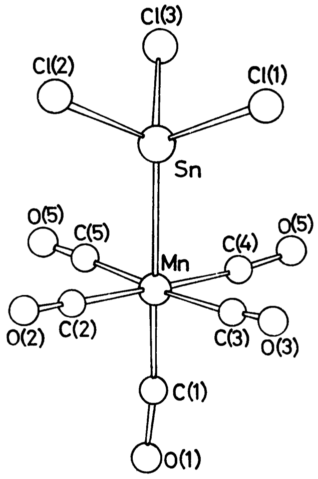

Fig. 1. The molecular structure of trichlorotin-pentacarbonylmanganese, Cl_3Sn–$Mn(CO)_5$.

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* Table 2 is kept as Document No. 7426 at the Chemical Society of Japan.

Table 4. Intramolecular distances (Å) and bond angles (°)

Bonds	Bond distances		Bonds	Bond angles		Bonds	Non-bonded distances (less than 4.0 Å)	
	Molecule 1	Molecule 2		Molecule 1	Molecule 2		Molecule 1	Molecule 2
Sn–Mn	2.575(5)	2.604(5)	Cl(1)–Sn–Mn	115.0(3)	117.6(3)	Sn······C(2)	3.14(5)	3.17(3)
Sn–Cl(1)	2.369(11)	2.334(11)	Cl(2)–Sn–Mn	118.5(3)	116.8(3)	Sn······C(3)	3.23(4)	3.15(3)
Sn–Cl(2)	2.302(12)	2.349(11)	Cl(3)–Sn–Mn	118.9(3)	117.3(3)	Sn······C(4)	3.15(5)	3.09(4)
Sn–Cl(3)	2.360(11)	2.362(12)	Cl(1)–Sn–Cl(2)	100.6(4)	100.3(4)	Sn······C(5)	3.12(4)	3.08(3)
Mn–C(1)	1.826(43)	1.913(35)	Cl(2)–Sn–Cl(3)	99.7(4)	101.2(4)	Cl(1)···Cl(2)	3.60(2)	3.59(2)
Mn–C(2)	1.873(47)	1.849(32)	Cl(3)–Sn–Cl(1)	100.8(4)	101.3(4)	Cl(2)···Cl(3)	3.56(2)	3.64(2)
Mn–C(3)	1.973(42)	1.877(29)	Sn–Mn–C(1)	179.0(14)	178.2(12)	Cl(3)···Cl(1)	3.65(2)	3.63(2)
Mn–C(4)	1.805(52)	1.832(36)	Sn–Mn–C(2)	88.4(14)	88.6(10)	C(1)···C(2)	2.64(6)	2.70(5)
Mn–C(5)	1.901(35)	1.885(32)	Sn–Mn–C(3)	89.3(12)	87.3(10)	C(1)···C(3)	2.68(6)	2.72(5)
C(1)–O(1)	1.183(49)	1.103(46)	Sn–Mn–C(4)	90.1(16)	86.7(12)	C(1)···C(4)	2.58(7)	2.71(6)
C(2)–O(2)	1.106(55)	1.148(45)	Sn–Mn–C(5)	87.0(11)	84.6(11)	C(1)···C(5)	2.72(6)	2.81(5)
C(3)–O(3)	1.061(49)	1.164(39)	C(1)–Mn–C(2)	91.2(20)	91.6(15)	C(2)···C(3)	2.73(6)	2.66(4)
C(4)–O(4)	1.147(59)	1.173(51)	C(1)–Mn–C(3)	89.8(18)	91.8(14)	C(3)···C(4)	2.66(7)	2.62(5)
C(5)–O(5)	1.126(44)	1.080(42)	C(1)–Mn–C(4)	90.4(21)	92.7(16)	C(4)···C(5)	2.61(6)	2.62(5)
			C(1)–Mn–C(5)	93.9(17)	95.2(15)	C(5)···C(2)	2.69(6)	2.61(5)
			C(2)–Mn–C(3)	90.2(19)	91.3(13)			
			C(2)–Mn–C(4)	178.4(22)	175.5(15)			
			C(2)–Mn–C(5)	90.7(18)	88.8(14)			
			C(3)–Mn–C(4)	89.3(20)	90.0(14)			
			C(3)–Mn–C(5)	176.2(16)	173.0(14)			
			C(4)–Mn–C(5)	89.7(20)	89.4(15)			
			Mn–C(1)–O(1)	174.1(36)	176.7(33)			
			Mn–C(2)–O(2)	176.2(41)	172.8(30)			
			Mn–C(3)–O(3)	175.6(37)	177.9(26)			
			Mn–C(4)–O(4)	173.0(44)	178.1(34)			
			Mn–C(5)–O(5)	177.2(31)	177.3(30)			

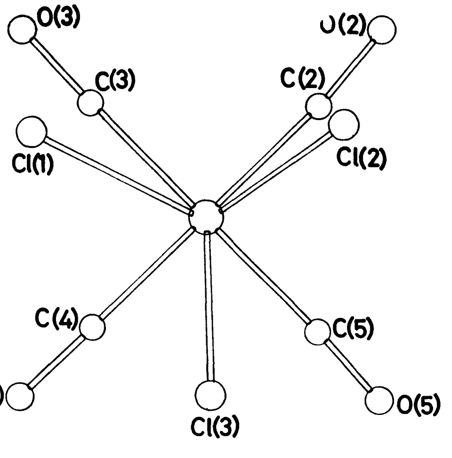

Fig. 2. A molecular view of $Cl_3Sn-Mn(CO)_5$ down the Sn–Mn axis from the Cl_3Sn moiety.

Table 5. Torsional angles

	Molecule 1	Molecule 2
Cl(1)–Sn–Mn–C(2)	108.7°	107.3°
Cl(1)–Sn–Mn–C(3)	18.8	16.8
Cl(1)–Sn–Mn–C(4)	71.3	72.7
Cl(1)–Sn–Mn–C(5)	161.2	163.2
Cl(2)–Sn–Mn–C(2)	10.3	11.7
Cl(2)–Sn–Mn–C(3)	100.2	102.2
Cl(2)–Sn–Mn–C(4)	169.7	168.3
Cl(2)–Sn–Mn–C(5)	79.8	77.8
Cl(3)–Sn–Mn–C(2)	131.6	131.8
Cl(3)–Sn–Mn–C(3)	138.5	137.6
Cl(3)–Sn–Mn–C(4)	48.4	48.2
Cl(3)–Sn–Mn–C(5)	41.5	42.4

and $(C_6H_5)_3Sn-Mn(CO)_5$ (2.674 Å).[10,11] This fact accords with our previous finding[1] that the Sn–Mn bond strength in $Cl_3Sn-Mn(CO)_5$ is greater than that of $(CH_3)_3Sn-Mn(CO)_5$. In order to correlate the Sn–Mn bonding-distance with the bonding nature, especially with the degree of the d_π-interaction between the tin and manganese atoms, let us examine the formula proposed by Pauling:[17]

$$R(\delta, Z) = 1.825 - 0.043Z - (1.600 - 0.100Z)\delta \quad (1)$$

where $R(\delta, Z)$ is the bonding radii of the metal atom concerned, Z is the effective nuclear charge (the number of electrons outside the rare-gas shell), and δ is the amount of the d-character in the bonding orbitals. The bonding radius of the manganese atom can be calculated as follows: if the single-bond radius of the chlorine atom in the Sn–Cl bond is assumed to be 0.99 Å,[18] the covalent radius of the tin atom is calculated to be 1.36 Å from the Sn–Cl bond distance in the present compound (mean, 2.35 Å). The subtraction of this value from the Sn–Mn bond distance leaves the value of 1.23 Å for the covalent radius of the manganese atom. In the same manner, we obtain 1.31 Å for the covalent radius of the manganese atom in $(CH_3)_3Sn-Mn(CO)_5$,[11] the single-bond radius of the methyl carbon being assumed to be 0.77 Å.[18] The application of these manganese radii to Pauling's equation yields δ values of 32.2 and 23.3% for Cl_3Sn–$Mn(CO)_5$ and $(CH_3)_3Sn$–$Mn(CO)_5$ respectively. The absolute magnitude of these values seems suspicious, because we used the value of 1.36 Å as the covalent-bond radius of the tin atom despite the usually-accepted covalent radius of the Sn(IV) of 1.399 Å. However, the most important feature is that the increased trend of the d_π-interaction going from $(CH_3)_3Sn$–$Mn(CO)_5$ to Cl_3Sn–$Mn(CO)_5$ predicted by normal coordinate analysis is clearly exhibited in the present results.

The results of normal coordinate analysis suggested also elongated Mn–C and shortened C–O bond distances in Cl_3Sn–$Mn(CO)_5$ compared with those in $(CH_3)_3Sn$–$Mn(CO)_5$. The finding that the mean Mn–C distance of the present molecule, 1.87 Å, is longer than that of $(CH_3)_3Sn$–$Mn(CO)_5$, 1.81 Å, is parallel to this prediction. However, the latter prediction is not clear, since the mean C–O distance, 1.13 Å, is close to the value, 1.15 Å, for $(CH_3)_3Sn$–$Mn(CO)_5$.

The mean Sn–Cl bond distance (2.35 Å) is equal to that of Cl_3Sn–$Fe(CO)_2(\pi$-$C_5H_5)$ (2.36 Å)[13] and slightly shorter than that of $Cl_2(C_6H_5)Sn$–$Fe(CO)_2(\pi$-$C_5H_5)$ (2.39 Å).[19] The observed Sn–Cl(2) bond distance in the molecule 1 is considerably shorter than the other Sn–Cl bond distances. It is not clear at present why this bond distance is shorter than the others.

Each molecule has an approximate mirror plane through the Cl(3)–Sn–Mn–C(1)–O(1) atoms. A slight rotation of the $SnCl_3$ moiety along the Sn–Mn bond about 3.9 ° for the molecule 1 and 2.8° for the molecule 2 leads to an exact mirror symmetry, and the rotational angles may be compared with those of 1° and 3.5° in $(CH_3)_3Sn$–$Mn(CO)_5$ and $(C_6H_5)_3Sn$–$Mn(CO)_5$ respectively.[10,11] Similar distortions are also observed in $(C_6H_5)_3Sn$–$Mn(CO)_4P(C_6H_5)_3$[12] and $(\pi$-$C_5H_5)Fe(CO)_2$–$Mn(CO)_5$.[20] There is a possibility that these distortions around the Sn–Mn axis are due to the Jahn-Teller effect, arising from the nonequivalence of ligands around the manganese atom.

Another interesting feature is that all the equatorial carbonyl groups are bent toward the tin atom with respect to the plane perpendicular to the Sn–Mn axis, the mean Sn–Mn–C (equatorial) bond angle being 87.8°. The diviations of the manganese atoms from the planes defined by four equatorial carbon atoms are 0.05 Å for the molecule 1 and 0.09 Å for the molecule 2. The equation of the least-squares plane is given by: $0.007X+0.940Y-0.341Z-3.464=0$ for the molecule 1 and $-0.106X+0.938Y+0.341Z-6.491=0$ for the molecule 2, where the coordinates X, Y, and Z, are in Å referred to the orthogonal axes, a, b, and c*. The same kind of distortion is observed in a number of molecules with direct metal-metal bonds: $(C_6H_5)_3Sn$–$Mn(CO)_5$,[10] $(CH_3)_3Sn$–$Mn(CO)_5$,[11] $(C_6H_5)_3Sn$–$Mn(CO)_4P(C_6H_5)_3$,[12] $(\pi$-$C_5H_5)Fe(CO)_2$–$Mn(CO)_5$,[20] $(C_6H_5)_2Sn[Mn(CO)_5]_2$,[21] $Hg[Mn(CO)_5]_2$,[22] $C_{15}H_{11}N_3$–$Cd[Mn(CO)_5]_2$,[23] and Br_3Ge–$Mn(CO)_5$.[9] The mean M–Mn–C (equatorial) bond angles in these compounds range from 87 to 83°. It seems that the steric effect of the substituents or the counter metal atom on M–Mn–C (equatorial) angles is unimportant. In earlier studies,[10,11] these distortions have been ascribed to the effect of molecular packing in crystals. Gapotchenko *et al.*, however, recently observed similar distortions even in an isolated molecule of Br_3Ge–$Mn(CO)_5$ by the electron-diffraction method.[9] The present author previously reported[4] that such distortion could also be expected in the case of Cl_3Sn–$Mn(CO)_5$ on the basis of the study of the dependence of the CO (equatorial) stretching IR intensity on the force constant, K(M–Mn), for a series of X_3M–$Mn(CO)_5$ molecules; he interpreted this relationship in terms of the interaction between the π^* orbitals of the four equatorial carbonyl groups and the M–Mn σ bond under the condition of the distorted M–Mn–C (equatorial) bond angle from 90°.

A distortion from the tetrahedral symmetry around the tin atom is usually observed in those compounds in which the tin atom is bonded to transition elements.[10–13)

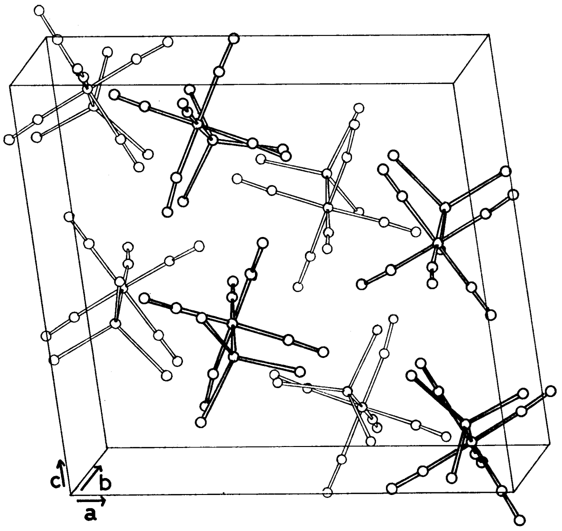

Fig. 3. Molecular packing in the unit cell.
Those molecules drawn by bold lines are located between 0 and 0.5*b* concerning the tin atom.

TABLE 6. SELECTED INTERMOLECULAR DISTANCES (Å) LESS THAN 4 Å BETWEEN THE BASIC MOLECULE AND ITS NEIGHBOURS.

The symmetry codes, I—XI, refer to the positions: I=(x, y, z), II=$(1+x, y, z)$, III= $(-1+x, y, z)$, IV=$(1-x, 1-y, -z)$, V=$(1-x, -y, 1-z)$, VI=$(1-x, 1-y, 1-z)$, VII=$(1-x, 1/2+y, 1/2-z)$, VIII= $(1-x, -1/2+y, 1/2-z)$, IX=$(x, 1/2-y, 1/2+z)$, X=$(x, 1/2-y, -1/2+z)$, and XI=$(1+x, 1/2-y, -1/2+z)$

Sn···O(5)(IX)	3.80(3)	Cl(3′)···C(3)(VIII)	3.64(4)
Sn′···O(4′)(X)	3.97(4)	Cl(1)···O(2′)(VII)	3.41(3)
Cl(1)···Cl(1′)(I)	3.57(2)	Cl(2)···O(5)(IX)	3.56(3)
Cl(1′)···Cl(3′)(V)	3.89(2)	O(4)···O(3′)(X)	3.07(4)
Cl(2)···Cl(2′)(II)	3.92(2)	O(2)···O(2′)(II)	3.13(5)
C(1)···Cl(2)(VII)	3.46(5)	O(3)···O(3′)(I)	3.13(4)
Cl(1)···C(1)(IX)	3.63(4)	O(5)···O(5′)(XI)	3.14(4)
Cl(1)···C(4)(IX)	3.69(5)	C(1′)···C(1′)(VI)	3.78(5)
Cl(1)···C(5)(IX)	3.69(4)	C(3′)···O(4)(IX)	3.36(4)
Cl(1′)···C(1′)(VIII)	3.54(4)	C(3)···O(5)(IX)	3.38(5)
Cl(1′)···C(2′)(VIII)	**3.54**(4)	C(1′)···O(1′)(VI)	3.39(5)
Cl(1′)···C(3′)(VIII)	3.63(3)	C(1)···O(1)(IV)	3.41(5)
Cl(3′)···C(1)(VIII)	3.54(4)	C(2′)···O(2)(III)	3.42(4)
Cl(3′)···C(4)(VIII)	3.56(4)	C(3)···O(3′)(I)	3.89(5)

Figure 3 shows the molecular packing in a unit cell.[24] Table 6 lists intermolecular atomic contacts less than 4 Å. The shortest one is 3.07 Å, between two oxygen atoms. This distance and the other minimum non-bonded intermolecular distances given in Table 6 correspond to normal van der Waals interactions. All these distances in Cl_3Sn–$Mn(CO)_5$ are rather shorter than those in the trimethyl analogue,[11] and the molecular packing of the present compound is more compact than that of the trimethyl compound. In those regions where chlorine and carbonyl groups come into contact, the chlorine atom tends to be located equidistant from the carbon atoms of the carbonyl groups, as may be seen in Table 6.

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