

## Chlorotris(pentacarbonylmanganese)tin

By J. H. TSAI,\* J. J. FLYNN, and F. P. BOER

(Exploratory Research Laboratory, Dow Chemical of Canada, Limited, Sarnia, Ontario, and the Eastern Research Laboratory, The Dow Chemical Company, Wayland, Massachusetts 01778)

A GENERAL understanding of the properties of metal-metal bonds will require further chemical, spectroscopic, and structural information for a variety of compounds. The direct Sn-Mn bond is at present one of the more intensively studied model systems.<sup>1-5</sup> We report here the properties and structure of a compound in which three Mn atoms are attached to a Sn atom through metal-metal bonds of lengths greater than hitherto reported.

A solution of SnCl<sub>4</sub> was added to a large excess of NaMn(CO)<sub>5</sub> in tetrahydrofuran. After removal of NaCl the resultant solution was evaporated to dryness *in vacuo* and the solid washed with oxygen-free water. Separation of the residue yielded red crystals, m.p. 177°, of empirical formula ClSnMn<sub>3</sub>C<sub>15</sub>O<sub>15</sub> (30-40%) and two other unidentified components. The first component is stable in air and in most organic solvents for a short time, and unlike other organotin halides, does not disproportionate with Me<sub>4</sub>Sn. With the infrared spectrum measured in cyclohexane [ $\nu(\text{C}\equiv\text{O})$ : 2082 ( $A_1^h$ ), 2038 ( $B$ ), 2022 and 2006 ( $E$ ), and

1991 cm.<sup>-1</sup> ( $A_1^h$ )]<sup>6</sup> we formulated this compound† as ClSn[Mn(CO)<sub>5</sub>]<sub>3</sub> and attributed the large splitting of the  $E$  mode (16 cm.<sup>-1</sup>) and the simultaneous appearance of the  $B$  band to the perturbing influence of the Cl atom.<sup>7</sup>

ClSn[Mn(CO)<sub>5</sub>]<sub>3</sub> crystallizes in the non-centrosymmetric monoclinic space group  $Pa$  with  $a = 17.95$ ,  $b = 9.08$ ,  $c = 15.02$  Å, and  $\beta = 107^\circ 55'$ . Each unit cell contains four molecules, and hence the structure determination requires the location of two independent molecules, or 70 atoms. Intensities of 2292  $X$ -ray reflections were estimated from Weissenberg and precession photographs taken with Mo- $K_\alpha$  radiation. The crystal structure was solved by a combination of Patterson and Fourier methods, and the atomic parameters were refined by least-squares,<sup>8a</sup> assuming individual isotropic temperature factors for the C and O atoms and anisotropic thermal parameters for Cl, Mn, and Sn, to the present value of  $R = 0.09$ .

The two molecules in the asymmetric unit have identical conformations, each with an apparent three-fold axis coincident with the Sn-Cl bond.

† Professor W. A. G. Graham has kindly informed us that he has independently prepared this material.

The bond angles about Sn are distorted markedly from tetrahedral values by the repulsion of the bulky  $\text{Mn}(\text{CO})_5$  groups. The average Mn–Sn–Mn angle is  $116.5^\circ$ , very nearly that observed<sup>4</sup> in  $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ , while the average Mn–Sn–Cl angle is  $101.0^\circ$ .

The mean Sn–Mn bond length of  $2.737 \text{ \AA}$  is considerably longer than the values<sup>4,5</sup> of  $2.70$  reported for  $\text{Ph}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$  and  $2.67$  for  $\text{Ph}_3\text{SnMn}(\text{CO})_5$ , in accord with a presumed trend to longer bond lengths with each successive  $\text{Mn}(\text{CO})_5$  substituent on Sn. Considerable differences were, however, found among the six individual Sn–Mn bond distances ( $2.720$ ,  $2.746$ , and  $2.753$  for the first molecule and  $2.703$ ,  $2.745$ , and  $2.758$  for the second). The individual standard errors for these Sn–Mn bond lengths, as calculated from the least-squares variance-covariance matrix are only  $0.006 \text{ \AA}$ . Because the computed individual standard errors for Sn–Cl, Mn–C, and C–O distances agree closely with the statistical errors calculated from redundant data, and because the short bond distance in each molecule is associated with the only  $\text{Mn}(\text{CO})_5$  group close-packed with Cl, we feel these differences may be significant<sup>8b</sup> and result from intermolecular crystal forces.<sup>3</sup>

The two Sn–Cl bond lengths of  $2.429$  and  $2.434 \pm 0.008 \text{ \AA}$  lie between the values in  $\text{Me}_n\text{SnCl}_{4-n}$  ( $2.33 \text{ \AA}$ )<sup>9</sup> and in  $[\text{Me}_2\text{SnCl, terpyridyl}]^+$  ( $2.63 \text{ \AA}$ ),<sup>10</sup> reflecting the reduction of *s*-character in the Sn–Cl bond. Whether this effect is caused by a tendency to  $sp^2$  hybridization of the Sn orbitals used in the metal–metal bonds resulting from steric distortion from a tetrahedron to a trigonal pyramid, or by the nature of tin–transition metal bonds in which the *s*-character of Sn orbitals was suggested<sup>2,11,12</sup> to be greater than the 25% implied in  $sp^3$  hybridization, has to be studied further.

The mean values of the thirty Mn–C and thirty C–O bond distances,  $1.81 \pm 0.01$  and  $1.16 \pm 0.01 \text{ \AA}$

respectively, are in good agreement with those reported<sup>14</sup> for  $\text{Mn}_2(\text{CO})_{10}$ , although no significant differences between axial and equatorial carbonyls could be detected.<sup>5</sup> Likewise, the average bond angle of the equatorial C atoms with the Sn–Mn axes was found to be  $86.9^\circ$  in agreement with the results<sup>5,13</sup> for related molecules.

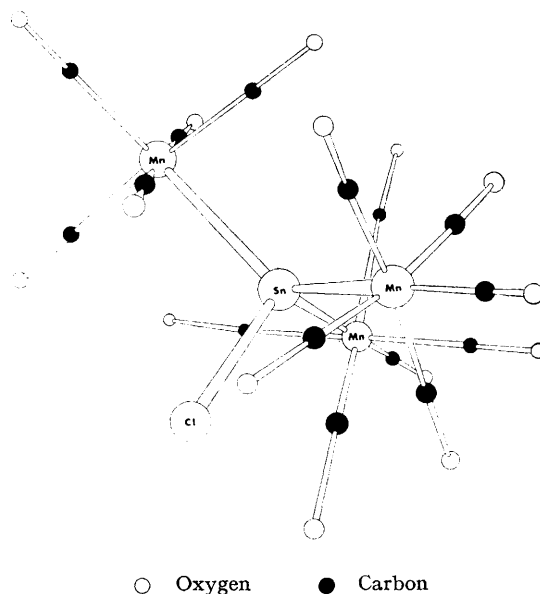


FIGURE. One of the chlorotris(pentacarbonylmanganese)-tin molecules as viewed in an *a* axis projection.

(Received, March 30th, 1967; Com. 309.)

<sup>1</sup> H. C. Clark and J. H. Tsai, *Inorg. Chem.*, 1966, **5**, 1407.

<sup>2</sup> W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2217.

<sup>3</sup> R. F. Bryan, *Proc. Chem. Soc.*, 1964, 232; *J. Chem. Soc. (A)*, 1967, 174.

<sup>4</sup> B. T. Kilbourn and H. M. Powell, *Chem. and Ind.*, 1964, 1578.

<sup>5</sup> H. P. Weber and R. F. Bryan, *Chem. Comm.*, 1966, 443.

<sup>6</sup> L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

<sup>7</sup> J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 384.

<sup>8</sup> (a) Refinement was carried out in blocks using the program OR FLS of W. R. Busing, K. O. Martin, and H. A. Levy (1962). Block refinement is required since the total number of atomic parameters, 328, exceeds the capacity of the IBM 7090 computer. In the final cycle the full matrix for all heavy atom parameters was included; (b) Systematic errors in the *X*-ray intensities due to absorption or anomalous dispersion are not believed to be large enough to account for these differences. Nevertheless, this explanation is always possible and is being investigated further.

<sup>9</sup> L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions", *Chem. Soc. Spec. Publ.*, No. 18, 1965, p. S12s.

<sup>10</sup> F. W. B. Einstein and B. R. Penfold, *Chem. Comm.*, 1966, 780.

<sup>11</sup> H. R. H. Patil and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1965, **87**, 673; *Inorg. Chem.*, 1966, **5**, 1401.

<sup>12</sup> J. H. Tsai, Ph.D. Thesis, University of British Columbia, 1965, p. 117.

<sup>13</sup> L. F. Dahl and R. E. Rundle, *Acta Cryst.*, 1963, **16**, 419.