

On the Structure of Methyl-
manganese Pentacarbonyl,
 $\text{CH}_3\text{Mn}(\text{CO})_5$

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There has been considerable discussion about the covalent radius of manganese. Pauling¹ pointed out the great difference in the single bond metallic radius (1.17 Å) and the radius (1.43 Å) calculated from the distance in gaseous Mn—H. The Mn—Mn bond length of about 2.92 Å found in $\text{Mn}_2(\text{CO})_{10}$ by Dahl and Rundle,² proved the smaller of these values to be unrealistic in compounds of this type. Recent estimates of the covalent radius range from 1.31 Å to 1.46 Å.³⁻⁵ Even though the wide range indicates that the concept of a covalent radius for manganese may be of limited value, a determination of the distance from methyl carbon to manganese in methylmanganese pentacarbonyl would be of considerable interest.

The compound was kindly supplied by Dr. T. H. Coffield, Ethyl Cooperation, Detroit. The electron-diffraction data were recorded on the Oslo apparatus.⁷ The electron wave-length was 0.064568 Å. Six photographic plates were recorded at a nozzle-to-plate distance of 48.046 cm, giving intensity data in the s range 1.75 Å⁻¹ to 19.875 Å⁻¹. We intend to record scattering data for higher angles. The data were treated in the usual way.⁸

The experimental radial distribution (RD) curve⁸ is shown in Fig. 1. The most

interesting molecular parameter, $C_{\text{met}}-\text{Mn}$, corresponds to the small peak near 2.20 Å. Several least-squares refinements have been carried out. To obtain reasonable estimates of the errors in the parameters, refinements were performed on each of the six intensity curves separately, as well as on the average curve.

Because of the limited s range it was not possible to refine the two different distances from manganese to carbonyl carbon ($\text{Mn}-C_{\text{ax}}$ and $\text{Mn}-C_{\text{eq}}$) independently. Previous investigations of dimanganese decacarbonyl⁹ and pentacarbonylmanganese hydride,⁵ indicate that the $\text{Mn}-C_{\text{ax}}$ distance is near 1.82 Å. The root-mean-square amplitudes of vibration (u) could not be refined for all the interatomic distances. Values for some of the non-bonded distances were assumed, when possible based on electron-diffraction results for dimanganese decacarbonyl⁹ or the amplitudes calculated from spectroscopic data for the same compound.¹⁰ The amplitudes for some distances were assumed equal, or to have a given difference (*cf.* Table 1).

Table 1 gives the results obtained by least-squares refinement on the average intensity curve. A diagonal weight matrix was applied, though it is known that the correlation between the data may be accounted for by including off-diagonal elements different from zero in the weight matrix.¹¹ One would therefore expect the standard deviations obtained in the least-squares refinement (σ_1 , in Table 1) to be unrealistically small. However, the agreement between the results obtained from each of the observed intensity curves is very satisfactory (*cf.* σ_2 in Table 1). On the other hand the results depend somewhat on the assumptions made in the re-

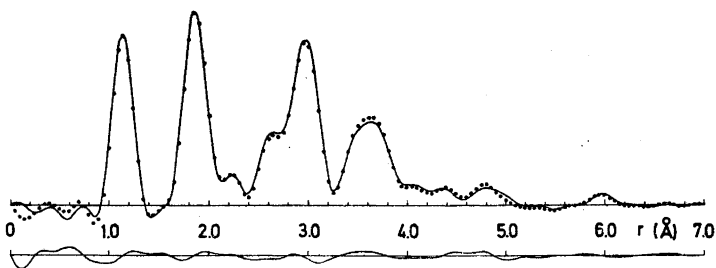


Fig. 1. Experimental (dotted) and theoretical RD curves obtained with an artificial damping constant equal to 0.003 Å². The curve giving the differences between experimental and theoretical curve is also shown.

Table 1. Results and standard deviations for the most important parameters in $\text{CH}_3\text{Mn}(\text{CO})_5$. Values found for $\text{HMn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$ are given for comparison.

	$\text{CH}_3\text{Mn}(\text{CO})_5^a$	σ_1^b	σ_2^c	$\text{HMn}(\text{CO})_5^d$	$\text{Mn}_2(\text{CO})_{10}^e$
$r(\text{Mn}-\text{C}_{\text{eq}})$	1.860 (4)	2	1	1.853 (12)	1.873 (5)
$r(\text{Mn}-\text{C}_{\text{ax}})$	1.820 ^f	—	—	1.822 (12)	1.803 (16)
$r(\text{Mn}-\text{C}_{\text{met}})$	2.185 (11)	11	4	—	—
$r(\text{C}-\text{O})$	1.141 (2)	1	1	1.134 (2)	1.147 (2)
$\angle \text{C}_{\text{ax}}\text{MnC}_{\text{eq}}$	94.7 (1.0)	1.0	0.1	94.9–98.9	93.4 (0.5)
$u(\text{Mn}-\text{C}_{\text{eq}})$	} 0.056 (4) ^g	3	2		0.052
$u(\text{Mn}-\text{C}_{\text{ax}})$					0.053
$u(\text{Mn}-\text{C}_{\text{met}})$	0.080 (13)	13	7		—
$u(\text{Mn}\cdots\text{O}_{\text{eq}})$	} 0.056 (4) ^g	3	2		0.052
$u(\text{Mn}\cdots\text{O}_{\text{ax}})$					0.053
$u(\text{C}-\text{O})$	0.028 (6)	5	2		0.035
$u(\text{C}_{\text{met}}\cdots\text{C}_{\text{ax}})$	0.105 ^h	} 6	2		—
$u(\text{C}_{\text{eq}}\cdots\text{C}_{\text{eq}})$ (short)	0.115 ^h				0.150
$u(\text{C}_{\text{ax}}\cdots\text{C}_{\text{eq}})$	0.135 ^h				0.163

^a Final results and standard deviations.

^b Standard deviations obtained by least-squares refinement with a diagonal weight matrix on the average intensity curve.

^c Standard deviations for the mean of six results, calculated giving the results the same weight.

^d See Ref. 5.

^e Distances and angles from Ref. 9, amplitudes from Ref. 10.

^f Assumed.

^g The amplitudes were assumed equal.

^h The differences between these amplitudes were assumed.

finement. The shift in the $\text{Mn}-\text{C}_{\text{met}}$ distance by changing the $\text{Mn}-\text{C}_{\text{ax}}$ distance by ± 0.01 Å was ± 0.001 Å. The torsional angle about the $\text{C}_{\text{met}}-\text{Mn}$ bond could not be determined. The values in Table 1 were obtained with the smallest $\phi(\text{C}-\text{Mn}-\text{C}-\text{H})$ angle equal to 15° . However, the results depended very little on this angle.

The theoretical RD curve shown in Fig. 1 was calculated with the parameters given in Table 1, neglecting shrinkage.¹² In the outer part of the curves the experimental peaks are slightly displaced towards lower r values compared to the theoretical peaks, indicating that the agreement might be improved by including shrinkage. Shrinkage values for $\text{C}_{\text{met}}\cdots\text{O}_{\text{ax}}$, $\text{C}_{\text{met}}\cdots\text{C}_{\text{ax}}$, and the longest $\text{O}_{\text{eq}}\cdots\text{O}_{\text{eq}}$, $\text{C}_{\text{eq}}\cdots\text{O}_{\text{eq}}$, and $\text{C}_{\text{eq}}\cdots\text{C}_{\text{eq}}$ distances, were assumed based on calculated values in $\text{Mn}_2(\text{CO})_{10}$,¹³ and included in a least-squares calculation. The agreement between experimental and theoretical data was somewhat improved. How-

ever, the results were very close to the values given in Table 1.

The final standard deviations (Table 1) have been estimated based on the results discussed above; the values are in no case less than σ_1 .

With a covalent carbon atom radius equal to 0.767 Å, the $\text{C}_{\text{met}}-\text{Mn}$ distance obtained in this study corresponds to a covalent radius of manganese of about 1.41 Å. This is in reasonable agreement with the estimate of 1.39 Å by Cotton and Richardson.⁴

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