

THE MOLECULAR STRUCTURE OF DECAMETHYLMANGANOCENE, $[\eta^5\text{-C}_5(\text{CH}_3)_5]_2\text{Mn}$, DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

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Summary

The molecular structure of decamethylmanganocene which is in the low spin state ${}^2E_{2g}$ in the gas phase, has been determined by gas phase electron diffraction. The equilibrium conformation is D_{5d} with staggered ligand rings. The Mn—C bond distance and root mean square vibrational amplitude are $r_a = 2.130(4)$ Å and $l = 0.076(4)$ Å, respectively.

Manganocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}$, is predominantly if not exclusively in the high spin state ${}^6A_{1g}$ in the gas phase [1]. The Mn—C bond distance determined by gas phase electron diffraction is $2.380(6)$ Å [2]. Decamethylmanganocene $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mn}$, on the other hand, appears to be exclusively in the low spin state ${}^2E_{2g}$ both in toluene solution at 313 K [3] and in the gas phase at 373 K [5]. The mean Mn—C bond distance obtained by X-ray crystallography is $2.112(2)$ Å [5], or more than a quarter of an Å unit shorter than in high spin manganocene.

1,1'-Dimethylmanganocene has been found to consist of a mixture of approximately equal amounts of high- and low-spin species both in toluene solution [6] and in the gas phase [1]. The Mn—C bond distance of the high spin species determined by gas phase electron diffraction [7] is $2.433(8)$ Å, i.e. significantly longer than in high spin manganocene. The Mn—C bond distance in the low spin species is $2.144(12)$ Å, and the magnitude of the Mn—C root mean square vibrational amplitude, $l = 0.160(16)$ Å, was interpreted as evidence for a dynamic Jahn-Teller effect involving the ring tilting mode [7].

We have now determined the structure of decamethylmanganocene by gas phase electron diffraction.

Experimental and structure analysis

$(C_5Me_5)_2$ was prepared as described by Robbins et al. [3]. The electron scattering pattern was recorded on Balzers Eldigraph KDG-2 with reservoir and nozzle temperatures of about 170°C . In order to keep the temperature as low as possible and thus avoid thermal decomposition, we used the scattering geometry suggested by Ivanov and Zazorin [8], which we have previously used when recording the scattering pattern of bis(neopentyl)magnesium [9].

Exposures were made with nozzle-to-plate distances of 50 and 25 cm. The optical densities of five plates from the first set and three from the second were processed using the programs described by Andersen et al. [10]. The complex scattering factors were calculated from an analytical representation of the atomic potential [11], using a program written by Yates [12]. The modified experimental molecular intensity data obtained by averaging the intensity values for each nozzle-to-plate distance ranged from $s = 2.25$ to 14.50 \AA^{-1} with increments $\Delta s = 0.125 \text{ \AA}^{-1}$ and from $s = 4.00$ to 26.00 \AA^{-1} with increments $\Delta s = 0.250 \text{ \AA}^{-1}$.

A molecular model of $(\eta^5-C_5Me_5)_2Mn$ with D_{5d} symmetry is shown in Fig. 1. It was assumed that the $C-CH_3$ fragments have C_{3v} symmetry and that the methyl groups are oriented as shown in the Figure. This is the orientation found in the crystalline phase [5]. The geometry is then determined by six independent parameters, e.g. the bond distances $C(1)-C(2)$, $C(1)-C(11)$, $C-H$ and $Mn-C$, the valence angle $\angle C-C-H$ and the angle between the $C(1)-C(11)$ bond and the C_5 ring plane, which we denote by $\angle C_5$, $C-C$ and define as positive when the bonds are bent towards the metal atom.

The $C(1)-C(11)$ bond distance and the $\angle C-C-H$ valence angle could not

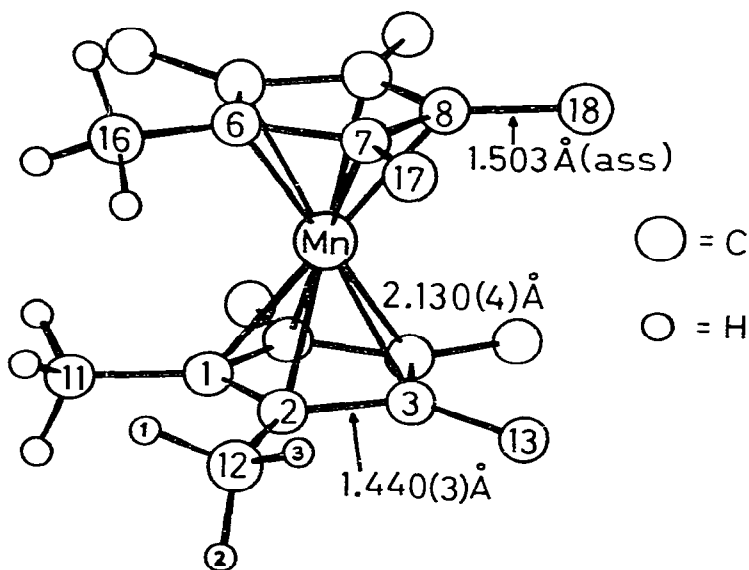


Fig. 1. Molecular model of $(C_5Me_5)_2Mn$. Symmetry D_{5d} (staggered ligand rings). Most of the hydrogen atoms have been omitted for clarity.

TABLE 1

INTERATOMIC DISTANCES, r_a , ROOT MEAN SQUARE VIBRATIONAL AMPLITUDES, l , FOR $(C_5Me_5)_2Mn$. (Estimated standard deviations in parentheses in units of the last digit)

	r_a (Å)	l (Å)		r_a (Å)	l (Å)
Mn—C(1)	2.130(4)	0.076(4)	C(1) --- C(6)	3.57	0.13(2) ^c
C(1)—C(2)	1.440(3)	0.052(5)	C(1) --- C(7)	4.01	0.12(2) ^c
C(1)—C(11)	1.503(ass)	0.053(ass)	C(1) --- C(8)	4.26	0.11(2) ^c
C(11)—H	1.114(6)	0.070(6)	C(1) --- C(16)	4.00	0.27(2) ^d
			C(1) --- C(17)	4.85	0.26(2) ^d
Mn --- C(11)	3.26	0.107(5)	C(1) --- C(18)	5.30	0.25(2) ^d
Mn --- H(1)	3.53	0.52(10)	C(11) --- C(16)	3.96	0.59(11) ^e
Mn --- H(2)	4.21	0.10(3)	C(11) --- C(17)	5.69	0.58(11) ^e
			C(11) --- C(18)	6.53	0.57(11) ^e
C(1) --- C(3)	2.33	0.061(7)			
C(1) --- C(12)	2.62	0.068(3) ^a			
C(1) --- C(13)	3.79	0.068(3) ^a	$\angle C-C-H = 112.4^\circ$ (ass)		
C(11) --- C(12)	3.21	0.137(10) ^b	$\angle C_5-C-C = -1.9(3)^\circ$		
C(11) --- C(13)	5.19	0.102(10) ^b	$h \uparrow = 1.743(4) \text{ \AA}$		

a, b, c, d, e groups of amplitudes refined with a fixed (assumed) difference. *f* h perpendicular distance from Mn to the center of the C_5 ring.

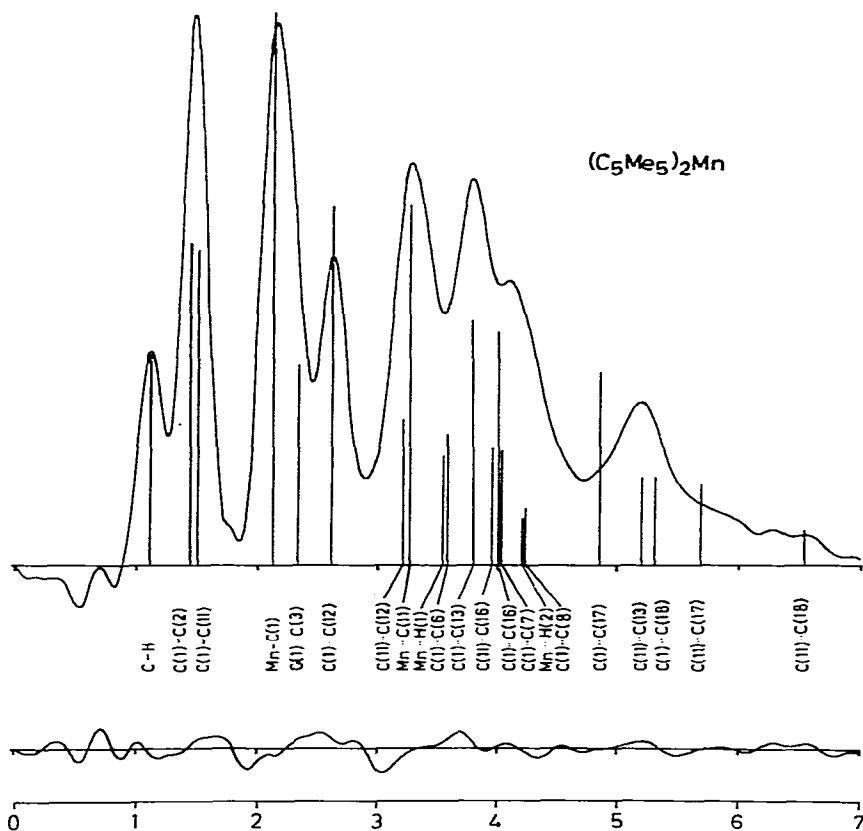


Fig. 2. Above: Experimental radial distribution curve for $(C_5Me_5)_2Mn$. Artificial damping constant $k = 0.002 \text{ \AA}^2$. Below: Difference between the experimental curve and a theoretical RD curve calculated for the best model.

be refined and were fixed at the values obtained in an electron-diffraction study of decamethylferrocene [13]. The remaining four structure parameters and the twelve root mean square vibrational amplitudes indicated in Table 1 were refined by least-squares calculations on the intensity data, using a program written by H.M. Seip [14]. The last cycles were calculated with a non-diagonal weight matrix and yielded the parameter values listed in the Table. The vibrational amplitudes have been corrected for the effect of the non-ideal scattering geometry as described in ref. 9.

A radial distribution curve calculated by Fourier inversion of the experimental intensity data is shown in Fig. 2 along with the difference between this curve and a theoretical curve calculated for the best model.

Refinements were also carried out with a model of D_{5h} symmetry, i.e. with eclipsed ligand rings. The resulting square-error sum was, however, nearly twice as high as for the staggered model ($R_2 = 14.1$ versus 7.4% [14]). An eclipsed model can therefore be ruled out with confidence.

Results and discussion

The equilibrium conformation of $(\eta\text{-C}_5\text{Me}_5)_2\text{Mn}$ in the gas phase is D_{5d} , i.e. with staggered ligand rings. This is also the equilibrium conformation of gaseous decamethylferrocene [13]. Both molecules retain this conformation in the crystalline state [5].

The structure of the C_5Me_5 ligand (see Table 1) is indistinguishable from the structure of the ligand in $(\eta\text{-C}_5\text{Me}_5)_2\text{Fe}$, and no significant differences are found between the intra-ligand vibrational amplitudes in the two compounds.

The Mn—C bond distance, 2.130(4) Å, is about 0.02 Å greater than found by X-ray crystallography, the difference is probably due to systematic errors introduced into the latter by lattice vibrations. The Mn—C bond distance determined by electron diffraction is not significantly different from the Mn—C bond distance in low spin dimethylmanganocene determined by the same method, 2.144(12) Å.

The Mn—C vibrational amplitude in $(\eta\text{-C}_5\text{Me}_5)_2\text{Mn}$, $l = 0.076(4)$ Å, is considerably smaller than in low spin dimethylmanganocene, $l = 0.160(16)$ Å. The large vibrational amplitude in the latter compound was interpreted as evidence for a dynamic Jahn-Teller effect involving the ring tilting mode [7]. It is possible that a similar Jahn-Teller effect in decamethylmanganocene is prevented by steric repulsion between the bulky methyl groups which are only 3.507(7) Å apart when the rings are parallel. But it also appears possible that the large amplitude in dimethylmanganocene reflects the asymmetry introduced by the two methyl groups (which by itself would break the degeneracy of the ${}^2E_{eg}$ state) rather than an inherent Jahn-Teller effect.

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