# Molecular Structure of High- and Low-spin 1,1′-Dimethylmanganocenes Determined by Gas Phase Electron Diffraction

By Arne Almenningen and Svein Samdal
(*Department of Chemistry, University of Oslo, Blindern, Oslo* 3, *Norway*)
and Arne Haaland
(*Department of Chemistry, University of Dar es Salaam, P.O. Box* 35061, *Dar es Salaam, Tanzania*)

*Summary* The molecular structures of high-spin ($^6A_{1g}$) and low-spin ($^2E_{2g}$) 1,1′-dimethylmanganocenes have been determined by gas phase electron diffraction; the Mn–C(Cp) bond distances are 2·42(1) and 2·14(2) Å, respectively.

While the electronic ground state of dicyclopentadienylmanganese, $Cp_2Mn$, is high-spin ($^6A_{1g}$),[1,2] the ground state of 1,1′-dimethylcyclopentadienylmanganese, $(MeCp)_2Mn$, is low-spin ($^2E_{2g}$).[2,3] The anomalous temperature dependence of the magnetic susceptibility of $(MeCp)_2Mn$ in toluene solution over the temperature range −59 to 98 °C has been interpreted in terms of a thermal equilibrium between the $^2E_{2g}$ ground state and the $^6A_{1g}$ excited state, and the enthalpy and entropy of reaction (1) has been determined as

$$(MeCp)_2Mn\ (^2E_{2g}) = (MeCp)_2Mn\ (^6A_{1g}) \qquad (1)$$

$$\Delta H^\circ = 7{\cdot}5 \pm 0{\cdot}4\ \mathrm{kJ\ mol^{-1}} \quad \text{and} \quad \Delta S^\circ = 24{\cdot}3 \pm 2{\cdot}5\ \mathrm{J\ K^{-1}}$$

mol$^{-1}$.[2] While the photoelectron spectrum of gaseous $Cp_2Mn$ at 60 °C can be successfully interpreted on the basis of a $^6A_{1g}$ ground state and no indication for the presence of low-spin species is found, the spectra of $(MeCp)_2Mn$ at the same temperature indicate the presence of high- and low-spin species in approximately equal amounts.[4] We now report the result of a gas phase electron diffraction investigation of $(MeCp)_2Mn$.

The electron diffraction pattern of $(MeCp)_2Mn$ was recorded from *s* 3·00 to 42·00 Å$^{-1}$ with a nozzle temperature of *ca.* 100 °C.

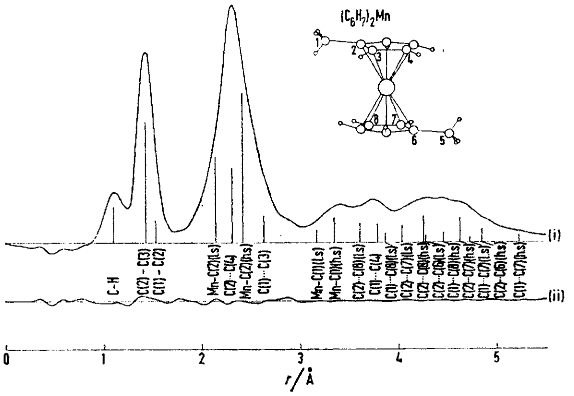

FIGURE. (i) Experimental radial distribution curve of $(MeCp)_2Mn$, and (ii) difference between the experimental curve and theoretical curve calculated for 'best models'. h.s. = high spin, l.s. = low spin.

A previous gas phase electron diffraction investigation of $Cp_2Mn$ which is predominantly, if not exclusively, in the high-spin state, has shown it to be a sandwich molecule with $D_{5h}$ (eclipsed rings) or $D_{5d}$ (staggered rings) symmetry.[5] Low-spin ($^2E_{2g}$) $Cp_2Mn$ is orbitally degenerate and suffers from a dynamic Jahn–Teller distortion.[6] However, gas phase electron diffraction investigations of two other metallocenes of first row transition elements with orbitally degenerate ground states, $Cp_2Cr$[7] which has a $^3E_{2g}$ ground state,[4] and $Cp_2Co$[8,9] which has a $^2E_{1g}$ ground state,[4] have shown that the electron scattering data can be successfully interpreted using models of effective $D_{5h}$ or $D_{5d}$ symmetry. It was therefore assumed that both low and high-spin $Cp_2Mn$ have effective $D_{5h}$ or $D_{5d}$ symmetry. Models for high- and low-spin $(MeCp)_2Mn$ were derived from those of the parent metallocene by replacing a H atom on each ring by Me groups. The structure of the MeCp ligands (interatomic distances and root mean square vibrational amplitudes) were assumed equal in the two states, but the Mn–C(Cp) bond distances and vibrational amplitudes as well as vibrational amplitudes between atoms in different rings were allowed to differ. The dihedral angle $\phi$ describing the relative orientation of the MeCp rings was defined as zero when the rings are eclipsed and the Me groups are *cis* and was assumed equal in the two states.

The mole fractions of high- and low-spin species, the two Mn–C(Cp) bond distances, five parameters determining the geometry of the MeCp ligands, and the fifteen most important vibrational amplitudes were refined by least-squares calculations on the intensity data[10] for a series of values of $\phi$. The best agreement ($R_2$ 5·8%[10]) was obtained for $\phi = 180°$, *i.e.* for staggered Cp rings and the Me groups *trans*. Refinements with other values of $\phi$ led to parameter values differing from those obtained for the 'best models' by <1·5 standard deviation.

The Figure shows (i) an experimental radial distribution curve calculated for $(MeCp)_2Mn$ and (ii) a difference curve calculated for the 'best models'.

The Mn–C(Cp) bond distance and vibrational amplitude obtained for high-spin $(MeCp)_2Mn$, *R*(Mn–C) 2·42(1) and *l*(Mn–C) 0·11(1) Å, are similar to those previously obtained for $Cp_2Mn$, 2·383(3) and 0·135(2) Å, respectively.[5]

The Mn–C(Cp) bond distance obtained for the low-spin state, *R*(Mn–C) 2·14(2) Å, is similar to the Co–C bond distance in cobaltocene, 2·119(3) Å.[8,9] In both compounds the electron imbalance is equal to one.[9] The M–C vibrational amplitude, *l*(Mn–C) 0·15(2) Å, is however considerably larger in low-spin $(MeCp)_2Mn$ than in $Cp_2Co$, *l*(Co–C) 0·082(1) Å. The reason for this apparent difference may be a Jahn–Teller distortion of low-spin $(MeCp)_2Mn$ so that the ten Mn–C bond distances are no longer exactly equal.

Finally we note that the mole fractions of high- and low-spin species obtained for the gas phase, $x_{hs}$ 0·63(5) and $x_{ls}$ 0·37(5), are in good agreement with those calculated from the magnetic susceptibility of $(MeCp)_2Mn$ in toluene at the same temperature, $x_{hs}$ 0·605 and $x_{ls}$ 0·395.[2]

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