Determination of the Mn–H Bond Length in $HMn(CO)_5$ by Gas-phase Electron Diffraction

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RECENTLY the value of 1·44 ±0·03 Å for the Mn–H bond length in manganese pentacarbonyl hydride, $HMn(CO)_5$, was provided by a reinterpretation[1] of the n.m.r. spectrum[2] of the compound in the solid state. We now report the result of a gas-phase electron diffraction study, which is in excellent agreement with this estimate.

Photographic data were recorded using the Balzers apparatus[3] at distances of 100, 50, and 25 cm., reduced by programs to be described elsewhere, and refined by a full-matrix least-squares program.[4] Off-diagonal weight matrices of the type suggested by Morino[5] were employed. The scattering amplitudes and phases were those calculated by Cox[6] by a partial wave summation.[7] In the experimental radial distribution curve $P(r)/r$, a peak was clearly apparent between 1·4 and 1·5 Å with an intensity appropriate for the Mn–H scattering. This peak is well resolved from the C–O peak at 1·136 and the Mn–C peak at 1·855 Å. The observed and difference (obs. − calc.) $P(r)/r$ curves are plotted (Figure). Least-squares refinement was carried out assuming the molecular point group C_{4v} with all C–O distances and all Mn–C distances respectively identical, and all Mn–C–O groups linear. These assumptions are justified by the crystal structure[8] and the reasonable Mn–C and C–O amplitudes obtained in this refinement. With the four geometrical parameters (C–O, Mn–H, Mn–C, and $C_{eq} \cdots C_{ax}$), the amplitudes of the three strongest peaks (C–O, Mn–C, and Mn ··· O) and three scale factors for the three camera geometries allowed to vary, the refinement converged to the structure given in the Table. The Mn–H amplitude and the non-bonded amplitudes were constrained to typical values [in most cases estimated from the calculations of Cyvin and Brunvoll on $Cr(CO)_6$ [9] and $Fe(CO)_5$ [10]].

It might be argued that the Mn–H bond length is affected by the fact that many of the amplitudes have been constrained. This is because the H ··· C and H ··· O peaks contribute to the estimate of the position of the hydrogen atom: these distances are overlapped in $P(r)/r$ (Figure) by other non-bonded distances, the amplitudes of which might be critical. We have therefore carried out statistical significance tests based on the R-factor ratio-distributions, which have been tabulated by Hamilton.[11] In a series of refinements the Mn–H distance was fixed at various points ranging from 1·15 to 1·75 Å, while all other variable parameters were refined to complete convergence. The variation of the generalised R factor shows a well defined minimum with r_{Mn-H} near 1·425 Å. From Hamilton's tables for 480 degrees of freedom we can establish the 99·5% confidence limits $1{\cdot}32\ Å < r_{Mn-H} < 1{\cdot}53\ Å$. This compares very well with the result of the direct refinement of $r_{Mn-H} = 1{\cdot}425$ Å (estimated marginal standard deviation 0·046 Å). The confidence limits are conservative in the sense that the excess of number of data points over number of refined parameters was in fact 663. We have also tested the five-rank hypothesis that the structure can be represented by a set of parameters where the Mn–H, H ··· C, and H ··· O amplitudes (five amplitudes in all) are fixed at 10 Å. The use of these extremely large amplitudes effectively removes all contributions involving the hydrogen atom from the calculated intensity altogether. This structure can be rejected at the 0·5% significance level, and it is therefore clear that the inclusion of the hydrogen atom results in an improvement which is statistically meaningful. We are investigating the refinement of further non-bonded amplitudes.

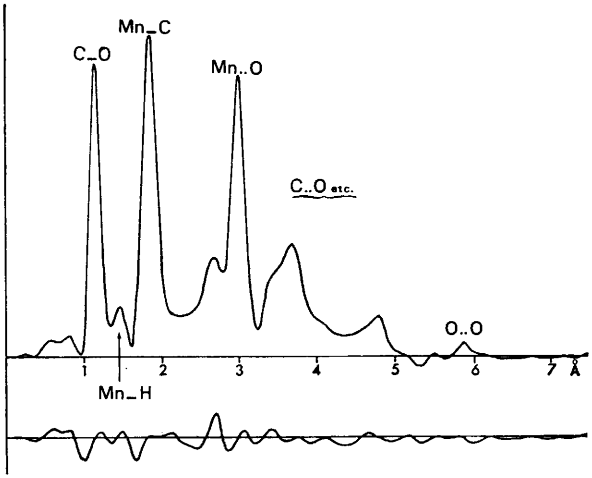

FIGURE. *Experimental and difference radial distribution curves,* $[P(r)/r]$ *for* $HMn(CO)_5$; *before the Fourier inversion the data were multiplied by* $[s.\exp(-0{\cdot}002\ s^2)/(Z_c - f_c)(Z_0 - f_0)]$.

The other geometrical parameters in the Table show satisfactory agreement with the results of the X-ray study[8] which gave r_{C-O} average = 1·130, r_{Mn-C} average = 1·836 Å ± 0·004 and $\angle C_{ax}MnC_{eq}$ average = 97·7°, especially since a libration correction is expected to increase the X-ray bond lengths by up to 0·015 Å.

TABLE

	Distance (Å)	Amplitude (Å)
r_{C-O}	1·137 ± 0·002	0·034 ± 0·008
r_{Mn-H} ..	1·425 ± 0·046	0·075 (fixed)
r_{Mn-C} ..	1·858 ± 0·001	0·066 ± 0·003
$r_{C_{ax} \cdots C_{eq}}$ ..	2·797 ± 0·004	0·085 (fixed)

$\angle (C_{ax}\text{–}Mn\text{–}C_{eq})$ 97·61° ± 0·17°

All uncertainties are estimated standard deviations.

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