Metal–Metal Interaction in the π-Cyclopentadienyltricarbonylmolybdenum–Pentacarbonylmanganese Complex, π-$C_5H_5Mo(CO)_3$–$Mn(CO)_5$

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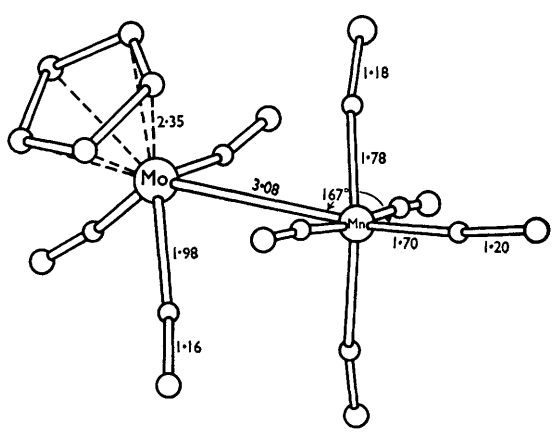
RECENTLY Hansen and Jacobson determined[1] the crystal structure of π-$C_5H_5Fe(CO)_2Mn(CO)_5$ (I), which may be envisaged as an adduct of the monomeric forms of $[\pi$-$C_5H_5Fe(CO)_2]_2$ (II) and $[Mn(CO)_5]_2$ (III), with Fe–Mn bond length 2·843 Å. The structure π-$C_5H_5Mo(CO)_3Mn(CO)_5$ is of interest due to its relationship to two closely analogous compounds, (III) and $[\pi$-$C_5H_5Mo(CO)_3]_2$ (IV), the structures of which are known.[2,3] Thus the primary purpose of the present investigation was to determine the Mo–Mn bond length and to establish the geometry of the molecule.

Crystal data. The red plate-like crystals, elongated along the *c*-axis, are monoclinic. Space group is $P2_1/c$, $a = 14{\cdot}62 \pm 0{\cdot}02$, $b = 8{\cdot}88 \pm 0{\cdot}01$, $c = 11{\cdot}62 \pm 0{\cdot}02$ Å, $\beta = 94 \pm 1°$, $U = 1510$ Å^3, $D_m = 1{\cdot}89$, $D_c = 1{\cdot}94$ g. cm.$^{-3}$ for $Z = 4$, $M = 439{\cdot}9$.

The intensities of *ca.* 1100 non-zero independent reflections were estimated visually from Weissenberg diagrams taken with unfiltered Cu-*K* radiation. An absorption correction was neglected.



FIGURE

The structure was determined by standard heavy-atom method and refined by full-matrix least-squares method with individual isotropic temperature factors. At present stage of refinement the

discrepancy index is $0{\cdot}14_3$ with an overall temperature factor $B = 5{\cdot}0$ Å^2 and the following standard deviations in bond length: Mo–Mn $\pm 0{\cdot}01$, Mo–C $\pm 0{\cdot}02$, Mn–C $\pm 0{\cdot}02$, C–O $\pm 0{\cdot}04$ Å.

The crystal consists of discrete molecules (see Figure) with the two moities held together solely by an Mo–Mn bond of length $3{\cdot}08 \pm 0{\cdot}01$ Å, which does not differ from the sum of the halved distances Mn–Mn and Mo–Mo in (III) and (IV) ($1{\cdot}462 + 1{\cdot}611 = 3{\cdot}073$ Å).

The arrangement of the carbonyls about the manganese atom is identical to that found in the structures (III) and (I). The equatorial carbonyl groups of the $Mn(CO)_5$ fragment have mean bond distances Mn–C 1·78 Å and C–O 1·18 Å, and for the axial group they are 1·70 Å and 1·20 Å, respectively. This shortening of the axial Mn–C bond has been found in (III) and (I): equatorial Mn–C 1·83 and 1·825 Å, axial Mn–C 1·79 and 1·749 Å, respectively. In the present structure the Mo–Mn–C_{ax} angle has a value 166·6° (the corresponding Fe–Mn–C_{ax} angle in (I) is 168·9°), whereas the Mn–Mn–C_{ax} angle in (III) is 180°.

The environment of the molybdenum atom is the same as that found in the previously studied complexes, containing the fragment π-$C_5H_5Mo(CO)_3$.[3,4] The mean Mo–C(cyclopentadienyl) distance 2·35 Å, Mo–C(carbonyl) 1·98 Å, and C–O 1·16 Å are normal.

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