The Structure of Tetrakis(organothiotricarbonylmanganese) and Related Compounds

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The nature of the products ultimately obtained by the reaction of thiols with manganese and rhenium pentacarbonyl bromides is currently in dispute. The polymers $[M(CO)_3{\cdot}SR]_x$ were originally[1,2] formulated as trimers in solution, but an unsymmetrical tetrameric structure has been suggested[3] on the basis of mass spectroscopy. We have shown that the correct structure in solution is in fact *symmetrically* tetrameric, by analysis of the combination spectrum. This conclusion applies to $[Mn(CO)_3SEt]_x$ (I), $[Mn(CO)_3S\text{-}p\text{-tolyl}]_x$ (II), and $[Re(CO)_3S\text{-}Ph]_x$ (III), and by implication to other compounds of this series.

In agreement with the earlier reports,[1,2] we find two strong i.r.-active bands in all these compounds [2017, 1944 in cyclohexane, 2016, 1942 in CCl_4 for (I)] with weak low-energy satellites, which we regard as ^{13}CO bands [2008 and ~1937 for (I)].

The combination spectrum of (I) in CCl_4 shows a large number of bands, proving that the paucity of active fundamentals is due to the operation of selection rules, rather than to accidental degeneracy. The entire combination spectrum may be assigned on the assumption of tetrahedral (T_d) symmetry, as follows: **4062** cm.$^{-1}$ ($A_1 + T_{2s}$), **4052** vw (^{13}CO), **4032** ($2T_{2s}$), **4012** vw (^{13}CO), **3988** ($A_1 + T_{2a}$), **3968** w ($E + T_{2s}$), **3960** ($T_{2a} + T_{2s}$), **3938** ($T_{2s} + T_1$), **3896** w ($E + T_{2a}$), **3890** ($2T_{2a}$), **3867** ($T_{2a} + T_1$), **3847** ($2T_1$). T_{2s} and T_{2a} are the two i.r.-active modes derived, respectively, from the a_1 and e modes of the individual $Mn(CO)_3$ units. A_1 is identified by its occurrence at high frequency,[4] while T_1 is distinguished from E by the activity of its overtone. The spectra of (II) and (III) are similar.

The only acceptable structure is then one in which the metal atoms form a regular tetrahedron, with a sulphur atom symmetrically situated above each face. A fuller analysis is in progress to try to estimate the degree of metal–metal bonding, and the number of electrons 'donated' by the sulphur atoms.

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