Preparation and Crystal Structure of [$Mn_4S_4(CO)_{15}$]; Oxidation at Sulphur of [{$(CO)_4Mn$-S-$SnMe_3$}$_2$]

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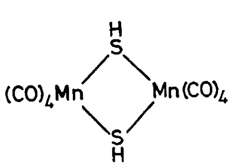
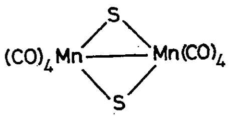
Summary The reaction of [{$(CO)_4Mn$–S–$SnMe_3$}$_2$] with iodine affords [$Mn_4S_4(CO)_{15}$], the crystal structure of which shows that dimerization and rearrangement have occurred during the oxidation.

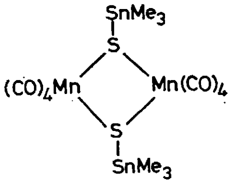
The redox chemistry of sulphur-containing transition-metal complexes is of importance in the context of metal–metal bonding[1] as well as biological electron transfer.[2] We therefore attempted to establish a transformation between the two stable dimanganese complexes (**1**)[3] and (**2**)[4] which had been obtained before by quite different routes. However, attempts to oxidize (**1**) to (**2**) by H_2O_2, I_2, azobisisobutyronitrile, or Me_2SO were unsuccessful.



(1)



(2)



(3)

Since Me_3Sn groups can be removed from S–$SnMe_3$ complexes by oxidation with iodine,[5] the reaction of (**3**),[6] which is also the precursor of (**1**), with iodine was investigated. The red crystalline product had an analytical composition which was consistent with that of (**2**). The i.r. spectrum in the CO region (in CCl_4: 2139w, 2090m, 2061vs, 2030sh, 2022vs, 2010s, 2007sh, 1985m, 1959m, 1951w, 1935w, and 1918w cm^{-1}), however, does not agree with that reported for (**2**).[4] The mass spectrum suggested a formula [$Mn_4S_4(CO)_{15}$] (**4**) which was subsequently confirmed by a crystal-structure analysis.

Crystal data: $C_{15}Mn_4O_{15}S_4$, M = 768·2, monoclinic, a = 9·288(5), b = 15·484(2), c = 18·162(25) Å, β = 96·02(8)°, U = 2597(3) Å^3, D_c = 1·96 for Z = 4, D_m = 1·96(1) g cm^{-3}, space group $P2_1/c$, Mo-K_α radiation, μ = 23·98 cm^{-1}. 3179 absorption-corrected independent reflections with $I \geqslant 3\sigma(I)$ were used in the calculation. The structure was solved by Patterson methods. Least-squares refinement resulted in an R factor of 0·041.

The Figure shows the molecular geometry of (**4**) with the two disulphide ligands linking the four manganese atoms. The Mn–S distances are normal (2·34—2·38 Å), as are the S–S distances (2·07 and 2·09 Å), and all manganese atoms

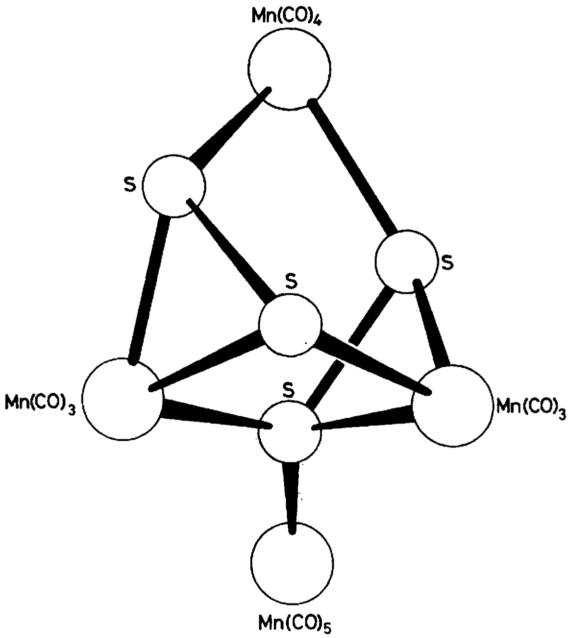
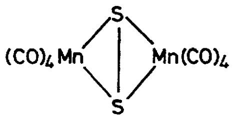


FIGURE. Schematic structure (heavy atom arrangement from the crystal structure analysis) of (**4**), $[Mn_4S_4(CO)_{15}]$.

achieve approximate octahedral co-ordination. Disulphide ligands with sulphur atoms bonding to one or two metal atoms have been observed before,[7] but the linking of three metal atoms as in (**4**) and the sulphur-bound $Mn(CO)_5$ group are unprecedented.

Whereas in other cases oxidation of two-metal–two-sulphur complexes promotes metal–metal bonding,[8] this does not seem to be the case with (**1**) and (**3**). Instead the formation of (**4**) represents the first case of generation of the disulphide ligand from complex bound mercapto groups. It can be assumed that (**5**) is the primary reaction product of (**3**) and iodine. Subsequent rearrangement of (**5**) to (**2**) seems to be impossible, and the release of steric strain from the unusual co-ordination of the sulphur atoms is achieved through dimerization of (**5**) accompanied by CO transfer and CO elimination. Within the molecular structure of (**4**), the two original Mn_2S_2 units, although partially distorted, can still be recognized.



(5)

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